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# THE CHEMISTRY OF SYNTHETIC RESINS

BY

CARLETON ELLIS

INDUSTRIAL RESEARCH CHEMIST

VOLUME I

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## Preface

The first edition of this book appeared in 1923 as *Synthetic Resins and Their Plastics*. The overwhelming number of synthetic resins and synthetic plastic products germinating in the twelve years intervening, together with the recognition of a broader knowledge of the causes and nature of resinification, have led to a change in the title of the present volume to *The Chemistry of Synthetic Resins*.

This, however, does not signify that any condensation or elimination of sections on plastics and plastic molding has occurred in the preparation of the second edition. On the contrary, the treatment of material on the subject has brought about a considerable expansion in the number of pages devoted to plastic molding.

Thus while a complete revision of the text has been required to provide the present edition, both the scientific and technical aspects of synthetic resins have, it is hoped, been given about equal weight. At the same time effort has been made to provide a complete literature survey of all species of synthetic resins.

Data, information and assistance have been received from so many sources that an impartial acknowledgment of all of these founts of information and help is difficult. My thanks, therefore, are given whole-heartedly to those (especially the members of my personal staff and of the Ellis-Foster Company) who have rendered assistance in one way or another in the completion of this exacting task, an undertaking the extent of which by comparison with the first edition clearly indicates the enormous degree of activity the past years have brought in the realm of synthetic resins.

CARLETON ELLIS

Ellis Laboratories  
Montclair, N. J.  
1935



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# THE CHEMISTRY OF SYNTHETIC RESINS

## Chapter I

### Introduction. Definitions. Classifications

On all sides the comment is heard that the present time constitutes the era of synthetic materials. The resources which nature provides now seem pitifully inadequate both in quantity and in quality to cope with the demands of industry and it is greatly to the credit of the scientist and more particularly to that of the chemist that the ever-increasing and varying demands of mankind can still be satisfied. The number of products which can be made from more elemental substances seems almost incredible. Naturally it is outside the scope of this book to consider them all but it is hoped that the present text provides a comprehensive survey of one important section—that of the chemistry of synthetic resins.

Progress in the synthetic resin industry can be said to have taken steps in two directions: (1) There has been a continuous development of new types of resins and (2) new applications have been made of the better-known materials. To adapt the more or less standard resinous products to new uses has necessitated, in some cases at least, modifications of various kinds.

The possible substitution of synthetic plastics for wood, metal and glass has received much consideration. The advantages of plastics have been repeatedly emphasized and are only too obvious. Cheap resins, as well as cheap methods of fabrication, are essential, however, before any extensive use can be made of molded or laminated products as structural materials. The manufacture of large molded cabinets and tanks and the employment of laminated board in table and desk tops and in wall paneling are dependent on the relative cost of these materials as compared with others now in use.

To produce a resin which promises any hope of commercial success, the chemist is limited to the use of relatively cheap raw materials—for example, phenol, urea, formaldehyde, glycerol, phthalic anhydride, acetylene, rubber and petroleum. For his laboratory preparation to remain other than a curiosity, it must have some properties superior to those of already existing products. In many cases the only apparatus required to make a synthetic resin is a test tube. This fact perhaps in part explains the cause of existence of several thousands of synthetic resins which have been reported and are discussed in the following pages. The huge number of recognized synthetic resins constitutes a figure which does not appear quite as disheartening, however, when it is realized that none of the known commercial synthetic resins is without a fault. There are usually one or more characteristics of a particular resin which preclude its application for some purpose to which other resins have been adapted. It is therefore evident that modifications of resins to improve their properties in one respect or another are necessary and must keep pace with the introduction of new types of resins of improved characteristics. Progress in the resin field, more so than in perhaps any other chemical industry, is largely conditioned by advances from the research laboratories.

Improvements in molding-technic have advanced the art of fabrication of plastics to such an extent that material costs of the molding composition are

now much more important than formerly. Among other things, perfection of automatic presses and mastery of the method of hobbing molds have reduced labor costs considerably. The introduction of injection molding methods is also in this direction. Cheaper molding compositions are therefore needed in order to keep pace with cost reduction on the mechanical side.<sup>1</sup>

Going back over the dozen years which have elapsed since the first edition of this book was published, one may enumerate the more important events in the field of synthetic resins as follows:

1. The expiration of certain patents on making and using phenol-formaldehyde condensation products has caused a greater diversification in the manufacture of these materials as well as a very substantial reduction in cost to the public.

2. A great concentration of effort has been applied to the development and production of certain resins of the phenol-formaldehyde type which would dissolve in drying oils to yield varnishes of an improved character. This effort has been productive of important results and having been contemporaneous with the rise of the nitrocellulose lacquer industry in the United States has, to a considerable extent, succeeded in putting a curb on the expansion of lacquers in the coating field. One great advantage arising in the use of lacquers was their quick-drying properties (since lacquers are generally made from nitrocellulose and resins dissolved in volatile solvents and the coating is dry as soon as the solvent has evaporated). Various forms of phenol-formaldehyde resins have, therefore, been brought forth which not only dissolve readily in drying oils but yield a varnish basis which when applied to a surface dries with comparative rapidity. This feat of increasing drying speed has given rise to numerous terms based on the rate of drying such as "2-hour" varnishes and "4-hour" varnishes. (See Chapter 19.)

3. The development and marvelous growth of alkyd resins, especially those containing a drying oil component, is another feature of the era. Alkyd resins are made by reaction between a polyhydric alcohol and a polybasic acid. For a great many years it has been known, as noted in the 1923 edition, "Synthetic Resins and Their Plastics," that a dibasic acid, typified by phthalic anhydride, and a polyhydric alcohol, illustrated by glycerol, would combine to form a resin, but it remained for the inauguration of the lacquer industry to stimulate research on the preparation of resins which would be compatible with nitrocellulose and produce durable lacquers. In the infancy of the lacquer industry the principal source of resin suitable for incorporation with nitrocellulose was dammar, the supply of which was limited and the quality variable because of the natural origin of the resin. The development of synthetic resins of the alkyd type supplied the lacquer industry with an adequate source of resinous material of uniform quality and such an abundance of compatible synthetic resin undoubtedly was in part instrumental in aiding the rapid expansion of this industry. A further development in the alkyd resin field is the type of resin in which a modifying agent is present to establish controlled resinification of the resin complex. The acids of drying oils were found adapted to the purpose. It is well recognized that drying oils lose much of their desirable siccative qualities if they are chemically changed or altered, yet the drying oil radical was found in the case of the alkyd resins still to be capable of drying. As a result these compositions, applied as coatings, yielded quick-drying finishes which were extremely durable even on outside exposure. Such compositions departed entirely from the usual lacquer formulation. Nitrocellulose was omitted. The drying oil alkyd resin was used alone dissolved in a cheap solvent instead of being mixed with nitrocellulose in a much more expensive solvent vehicle. Despite the profound alteration of the drying oil

<sup>1</sup> Carleton Ellis, *Ind. Eng. Chem.*, 1934, 26, 37.

glyceride molecule by resinification, the high rate of drying of this type of siccative resin was striking. (See Chapters 41-49.)

4. The introduction of chlorinated rubber under the trade name of Tornesit has provided the coating industry with another material for making paints or varnishes of unusual resistance to alkali and acids. (See Chapter 55.)

5. The recrudescence of vinyl resins also should be noted. These had been fairly well studied at the time the first edition of the book was published in 1923, but commercial development was lacking. In the intervening years, however, several large companies have undertaken the manufacture of vinyl resins and the output is becoming substantial. (See Chapters 51-52.)

6. The rapid rise of urea resin molding compositions is another characterizing feature of the past twelve years. Beginning, in the first instance, with unproductive efforts to make clear glass-like articles which would be permanent, the industry eventually developed in the molding field, since the absence of dark colors in the resin enabled attractive new shades of molded goods to be placed on the market. This development was stimulated by the fact that urea resins could be rendered thermosetting and could therefore compete with many of the phenol-formaldehyde products. The urea resins possess an advantage over the phenolic resins in that molded articles can be made which enjoy a degree of translucency greatly superior to that of the phenol-formaldehyde molded goods. The light-stable qualities of the urea resins, coupled with the ability to make the delicate pastel shades which hitherto had been denied the industry by phenolic resins, created an unprecedented demand for the products made from urea sources. (See Chapters 26-32.)

It is not intended from the foregoing to imply that the natural resins lack many useful properties. On the contrary, some of them, e.g., shellac, have been difficult to duplicate in the quality of hardness and toughness. (See Chapter 2.) Yet there is a limit to the supply of the best qualities of natural resin. In consequence they are subject to adulteration and to price fluctuation. The search for substances to replace the natural products was instigated many years ago with a view to having a guaranteed quality of material at hand, thereby overcoming these two serious drawbacks. Correlated problems naturally arose from these researches, soon to assume major significance. The discovery of a class of fusible resins which when heated above a certain critical temperature formed infusible as well as insoluble resins is one such instance. Some of these products, generally designated as thermosetting resins, are now, as is well known, the basis of the resin-filler molding powders.

An idea of the rapid growth of the synthetic resin industry is obtained by a study of Table 1 which has been compiled from various sources.<sup>2</sup>

In discussing the subject of synthetic resins it is of course necessary to define a resin. One cannot rely solely on the picture presented by the thought of the familiar natural resins since the common synthetic resins have very little resemblance to the natural resins. It is probable that for this reason the term "synthetic plastic" has often been used when speaking of synthetic resins. However, as is pointed out later, plastics include a much broader field.

A resin may be defined as a solid or semi-solid, complex, amorphous mixture of organic substances, having no definite melting point and showing no tendency to crystallize. A resin is characterized by such physical properties as a typical luster and a conchoidal fracture rather than by any definite chemical composition.<sup>3</sup>

<sup>2</sup> O. Wilson, *Ind. Eng. Chem.*, 1927, 19, 917; 1933, 25, 227. J. N. Taylor, Report of Chemical Division, U. S. Bureau of Foreign and Domestic Commerce, 1933. See also *Chem. Age* (London), 1929, 20, 523; 1931, 24, 418; 1932, 26, 52. *J.S.C.I.*, 1928, 47, 1270; 1930, 52, 662. *Literary Digest*, 1932, Jan. 2, 40.

<sup>3</sup> It is interesting to note the derivation of the word "resin." The word is probably derived

TABLE 1.—Production of Synthetic Resins in the United States.\*  
1920-1933

Year	Tons Produced	Year	Tons Produced
1920.....	2000	1927. . . . .	7,500
1921.....	800	1928 . . . . .	10,000
1922.....	3000	1929 . . . . .	16,500
1923.....	3500	1930.....	15,500
1924.....	5000	1931. . . . .	17,500
1925.....	6000	1932. . . . .	15,500
1926.....	6000	1933.....	22,500

\* The figures for 1920-1926 are for phenol resins only. Those for 1927-1931 are for resins of coal-tar origin only. About 60-65 per cent of the latter can be considered phenolic. The 1932 production is distributed as follows: Coal-tar origin, 14,500 tons; Non-coal-tar origin, 1000 tons. The production for 1933 was divided thus: Phenol, 12,500 tons; Phenol-resol, 3250 tons; Alkyd 5000; Urea or thiourea, 1600; All others, 150 tons. For purposes of comparison 6500 tons of pyroxylin plastics were produced in 1933.

The term "resin" was originally applied to the natural resins which occur in certain plant secretions.<sup>4</sup> The naturally occurring resins are for the most part light-colored vitreous substances, perfectly hard or at most only slightly sticky at ordinary temperatures, but capable of softening or melting when heated. They are insoluble in water but can be made to dissolve in certain organic solvents.<sup>5</sup>

A synthetic resin is merely, as the name implies, a resin formed by synthesis, using non-resinous organic materials as reactants. Synthetic resins do not necessarily possess the same properties as the natural resins. It is for this reason that the term "synthetic resin" is preferred to "artificial resin." An artificial resin would be one made to imitate a natural resin in its properties whereas a synthetic resin can possess properties which are entirely its own. The term "synthetic balsam" has come into use to designate the synthetic resins which are of the nature of viscous syrups, analogous to the naturally-occurring oleoresins and balsams. Thus the field of synthetic resins covers a group of organic materials ranging from viscous liquids to hard, infusible amorphous solids.

In the broadest sense the various bitumens, tars and pitches must be included as resins. It is of course difficult to define specifically the words "bitumen," "tar," "pitch," etc., since in common usage the terms are somewhat interchangeable. This is only natural because these substances are very similar in chemical and physical characteristics.

The international definition for *bitumen*<sup>6</sup> decided upon in 1928 states that it is a generic term for the "mixtures of natural and pyrogenous hydrocarbons and of their non-metallic derivatives, which may be either gaseous, liquid, viscous or solid, but must be completely soluble in carbon disulphide." In popular usage only the solid or viscous-liquid bitumens have been included in the definition. The solid or semi-solid bitumens containing only a small proportion of volatile constituents are now called *asphaltic bitumens*.<sup>7</sup> *Asphalt* is defined as a natural or mechanical mixture of solid or viscous bitumens with inert mineral matter.<sup>8</sup>

from the Latin word *rasis* and the Greek word *rhasis*. The Latin *rasis* means "a kind of rough powdered pitch used to mix with wine," thus denoting one of the early uses of natural resins. The Greek *rhasis* is a gradation variant of *rhetine*. The letter combinations *re* and *rhe* are from a word meaning "to flow." This can be seen in the prefix *rheo* and the word *stream*. "Universal Dictionary of the English Language," E. P. Dutton and Co., New York, 1932.

\* A notable exception is shellac, which is exuded by an insect rather than by a plant. See Chapter 2.

<sup>5</sup> Natural resins are often called "gums" or "gum resins" by the varnish maker. They are not true gums, however. The true gums are also excreted from plants but they are water-soluble, or at least form gels in water, and are insoluble in alcohol. Gum arabic and gum tragacanth are examples of true gums.

<sup>6</sup> W. J. A. Butterfield, *J.S.C.I.*, 1928, 47, 294T.

<sup>7</sup> An account of the various uses of solid and semi-solid bitumens is given by T. Temme, *Asphalt u. Teer*, 1934, 10, 167; *J. Inst. Pet. Tech.*, 1934, 20, 432A.

<sup>8</sup> F. J. Nellensteyn (*J. Inst. Petroleum Tech.*, 1924, 10, 320; 1928, 14, 134) concludes that asphalt contains elementary carbon in colloidal form as its essential constituent.

*Tars* are the viscous liquids obtained in the destructive distillation of organic substances (e.g., wood tar, coal tar). Their composition is of course dependent upon the initial materials and the temperature of distillation. *Pitch* is the black or dark brown, solid or semi-solid residue obtained by the partial evaporation or fractional distillation of a tar.<sup>9</sup>

Synthetic resins are often referred to as plastics, thus denoting that one of their uses is as molding material. Plastics of course include all substances capable of being worked and molded (e.g., clay, plaster, cement, putty, metals). Naturally such a broad field is not to be covered in this book. Such organic plastics as nitrocellulose, cellulose acetate and casein are likewise outside the scope of synthetic resins. It may be argued that these substances are resins according to the



Courtesy Bakelite Corp.

FIG. 1.—Compounding Polystyrene with Coloring Agents.

definition given, but at the same time they are not truly synthetic resins but are modified natural products.<sup>10</sup>

The term "plastic" is applied to anything which possesses plasticity; that is, anything which can be deformed under mechanical stress without losing its coherence and is able to keep the new form given it.<sup>11</sup> It is often stated that the term "plastics" as applied to the molded articles on the market is a misnomer since such rigid materials are anything but plastic. The term is applied in the industry to those materials (i.e., cellulose nitrate, cellulose acetate, casein, synthetic resins) which are in a plastic state during some part of their manufacture.<sup>12</sup> It is obvious that materials which are plastic at ordinary temperatures

<sup>9</sup> See D. M. Wilson, *J.S.C.I.*, 1924, 3, 924. H. Abraham, *Ind. Eng. Chem.*, 1913, 5, 11. J. Le Braz, *Glaces et verres*, 1934, 538, 4; *Chem. Abs.*, 1934, 28, 6991.

<sup>10</sup> Some exception is made to this ruling, however, and such materials as modified natural resins (Chapters 37-39) and modified rubber (Chapters 54-55) are discussed in this book.

<sup>11</sup> Plasticity is discussed more fully in Chapter 3.

<sup>12</sup> See J. Obrist, *Kolloid-Z.*, 1928, 45, 82; *Chem. Abs.*, 1928, 22, 4208. C. Stark, *Gummi-Ztg.*, 1931, 45, 1242; *Chem. Abs.*, 1931, 25, 3778. W. J. Jenkins, *J.S.C.I.*, 1933, 52, 241. H. C. Parker, *J.S.C.I.*, 1933, 52, May 19, 818.

will not form useful molded articles. Hence substances are used which are either thermoplastic or thermosetting.<sup>13</sup>

A thermoplastic substance is one which is adequately rigid at normal temperatures and under ordinary conditions of stress but is capable of deformation under heat and pressure. This property is permanent in a thermoplastic substance; that is, the process of deformation under these conditions can be repeated. In contrast to this is the term "thermosetting" or "thermohardening." A thermosetting substance is one which possesses initially the properties of a thermoplastic but which under the influence of heat undergoes chemical change so that it is no longer thermoplastic but is permanently infusible. In the case of synthetic resins there are two types of thermosetting materials. The quick-thermosetting resins (e.g., phenol-aldehyde and urea-aldehyde) undergo rapid chemical change to an infusible form during the molding process. The slow-thermosetting resins require considerable time for conversion to an infusible condition.

It is of course obvious that the quick-thermosetting type of resin is always sought for in molding operations since the process is speeded up considerably in this case. In molding a thermoplastic material it is necessary to cool the mold every time in order to avoid distorting the finished article, but in the use of a thermosetting material the molded piece can be removed without any preliminary cooling. The speed with which the molding can be done depends greatly on the time taken for the hardening operation.

#### CLASSIFICATION OF RESINS

The various methods of classification of synthetic resins fall into three groups: by physical characteristics, by chemical characteristics and by initial reacting materials. The last-named method is the one employed in the present work. A perusal of the table of contents shows that the general order of starting materials is as follows: hydrocarbons, phenols, aldehydes, ketones, amines, natural resin acids, polyhydric alcohols and polybasic acids, vinyl compounds, rubber, sulphur and fatty oils. This sort of classification is necessary because of the large number of resins reported and because most persons are familiar with resins from such standpoint.

In the classification adopted by Kienle<sup>14</sup> synthetic resins are grouped according to their behavior after the initial condensation. There are three main divisions:

1. **Heat-convertible resins.** Those which become infusible by the action of heat. Included in this group are the glycerol-polybasic acid resins, acetylene derivatives, polyolefin resins and the phenol-aldehyde resins.

2. **Heat-nonconvertible resins.** Those which remain thermoplastic. Examples are the glycol-polybasic acid resins, vinyl resins and certain of the phenol-aldehydes (acid type).

3. **Element-convertible resins.** Those which become infusible through the action of certain elements such as oxygen or sulphur. This group includes the glycerol-polybasic acid-drying oil resins<sup>15</sup> and olefin-sulphur resins.

Synthetic resins may also be classified as:

##### A. Monomeric

E.g., phenolphthalein, aroclors.

<sup>13</sup> The term "resin" is restricted by some to thermoplastic resins, and the word "resinoid" is used to designate the heat-hardening resins. See H. L. Bender, H. F. Wakefield and H. A. Hoffman, *Chem. Reviews*, 1934, 15, 123; *Chem. Abs.*, 1934, 28, 7042.

<sup>14</sup> R. H. Kienle, *Ind. Eng. Chem.*, 1930, 22, 590. See also Chapters 4 and 41.

<sup>15</sup> See Chapter 44.

**B. Polymeric****1. Linear macromolecules**

E.g., vinyl resins, polystyrene, polyindene, novolacks and heat-nonconvertible alkyds.

**2. Tridimensional macromolecules**

E.g., heat-convertible alkyds, phenol-aldehyde resins, urea-aldehyde resins and the drying oil alkyds.

Another method of classification is that used by Carothers.<sup>16</sup> Polymers are divided into two classes:

**1. Addition or A polymers.** In this class the molecular formula of the monomer is identical with that of the structural unit. Included here are polyolefins, polyoxymethylenes, polystyrene and unsaturated hydrocarbons.

**2. Condensation or C polymers.** In this type the molecular formula of the monomer differs from that of the structural unit. Examples are polybasic acid-polyhydric alcohol esters, phenol-aldehydes, urea-aldehydes, etc.

The importance of the field of synthetic resins is indicated by the large number of articles which have appeared on the subject. The appended list includes a great many of the general reviews already published.

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## Chapter 2

### Need for Synthetic Resins and Types Desired

As was pointed out in Chapter 1, the principal motive in creating synthetic resins is not to imitate the natural products but to improve on them. As wonderful and useful as the natural resins are there is not one that is entirely perfect and all of them have faults which should be eliminated. Then too, the day must be faced when the supply of natural resins will be exhausted; and even before that, the time when the best specimens are gone and only inferior grades remain.<sup>1</sup>

In the development of many fields in which synthetic materials are to replace natural ones the first step is to imitate the natural product, but later the trend is toward the creation of substances never before encountered. Witness, for instance, the dye industry which has grown to enormous proportions. The first accomplishment was the actual synthesis of the naturally occurring product and later the imitation of natural colors. Finally with increasing discoveries entirely new dyes were produced which were far superior to anything to be found in nature. In the case of synthetic resins the same trend is not only possible but has actually taken place. The search is now for resins having properties not possessed by any material in existence. In spite of all the resinous products mentioned in this work, very few have many desirable properties and not one is perfect.

A large use for natural resins has been in protective and decorative coatings, i.e., varnishes and lacquers. Of course there have been numerous other uses including the forming of molded articles, adhesives and fabric-impregnating materials. In the case of shellac, more than half of the amount produced is employed in moldings, principally for phonograph records. As has just been stated, however, the natural resins have been used mainly in varnishes. There are two principal types of varnishes, oil varnishes and spirit varnishes. The latter type, the spirit varnish, is merely a solution of a resin in a volatile solvent. Drying in this case involves the evaporation of the solvent, leaving the resin as a film on the surface to which the varnish has been applied. In a drying-oil varnish the oil and the resin together give the desired film. The oil itself on drying would supply a tough elastic film which however lacks sufficient hardness and gloss. The resin, on the other hand, when used alone may lack toughness and elasticity, but it imparts to the varnish film the necessary hardness and gloss and frequently improves atmospheric resistance.

The fossil resins at first glance appear almost perfect for varnishes because of their hardness and high gloss, but the disadvantage arises from the fact that they are insoluble in drying oils, owing to their high degree of polymerization.

<sup>1</sup> According to A. J. Gibson (*J.S.C.I.*, 1933, 52, (May 19), 88) the annual world-production of natural resins is approximately 750,000 tons. This is distributed roughly as follows: Rosin, 600,000; Copal, 36,000; Shellac, 32,000; Dammar, 11,000; Kauri, 5000; Acroïdes, 1200.

Among the various books dealing with natural resins may be mentioned: R. S. Morrell, "Varnishes and Their Components," D. Van Nostrand, New York, 1923. H. Wolff, "Die natürlichen Harze," Wissenschaftliche Verlags-G.m.b.H., Stuttgart, 1928. H. Hadert, "Tropische Lackrohstoffe," O. Elsner Verlags-G.m.b.H., Berlin, 1932. T. H. Barry, "Natural Varnish Resins," E. Benn, London, 1932. A. Tschirch and E. Stock, "Die Harze," Gebrüder Borntraeger, Berlin, 1933.

The resins must first be subjected to a melting process, known to the trade as "running," in order to render them soluble in drying oils. The result of the running is a depolymerization and a partial decomposition into oily constituents, causing a small, though not serious, loss of hardness. The difficulties encountered in using oil varnishes are evident. The work of "running" the varnish resin, adding driers and thinners, maturing and filtering could all be eliminated if a resin could be found which needed merely to be dissolved in appropriate solvents and applied to surfaces to form durable films.\* Another difficulty found in the use of oil varnishes is the long time required for the drying of the film. This is of course eliminated in the spirit varnish or lacquer. In this case the characteristics of the film depend on the resin or cellulose compound used. Thus far, however, few substances have been found which possess luster and hardness and at the same time are tough and elastic.

Hence the work on new coating compositions is toward more rapidly drying varnishes which give tough lasting films. This work can be carried out along at least two different paths.

(1) Incorporate a drying element within the synthetic-resin molecule. This has already been tried with remarkable results in the drying oil-polyhydric alcohol-polybasic acid resins. (See Chapter 44.)

(2) Synthesize a resin soluble in a cheap solvent which on evaporation leaves a hard, tough enduring film.

It may well be said that as yet the coating industry has not found the perfect resin. For coating compositions the ideal resin must not only possess the sum total of all desirable physical properties demanded of a film-forming material, but must also present economic advantages in its production and in its use. The cost of the resin is not the entire consideration. More important is the cost of the final film; that is, solvents are of prime importance.

Accordingly, the present trend of the coating industry is towards the development of a resinous substance of suitable properties, the one requisite of which is that it must be soluble in cheap solvents. Moreover, the resin should not retain the solvent in a tenacious way. On the application of a coating solution, the solvent should evaporate freely, at least to the degree where the film becomes dry and hard.

Other properties wished for in the resin, or properties which should be obtained through admixture with other materials, are that it must be of proper color and it must give films of proper gloss and adhesion. The melting point must be high enough so that no softening occurs under ordinary rise of temperature. The flexibility must be such that no cracking takes place at low temperatures, the film remaining free from brittleness. The film must be hard enough to wear well and resist abrasion. It must be waterproof, heat-resistant, noninflammable, and light-stable. It should resist alkalies, acids and other reagents, and should satisfactorily combat corrosion. Change to an insoluble form shortly after application also is desirable. The film should undergo little or no progressive change on aging such as is encountered with ordinary drying oil paints where continued oxidation occurs with consequent volume changes and chalking. All these qualities may be comprised in the condition that the resin must produce films which are light-colored, tough and durable.

In addition to a search for the perfect resin more study must be made on the causes of defects produced in varnish films, sometimes through no fault of the resin itself but through the wrong method of application, the wrong choice

\* See Carleton Ellis, *Ind. Eng. Chem.*, 1933, 25, 125.

of solvents or mistakes in preparing the surface to be coated. Gardner<sup>3</sup> has classed the causes of opacity in films into 3 groups.

1. The action of actinic rays. This may lead either to a chemical decomposition or to physical changes resulting in a lowering of the elasticity or a decrease in hardness.

2. The production of heterogeneity in a film during drying through the precipitation of solid matter. This difficulty arises principally from differences in the rates of evaporation of solvents. When mixtures of solvents are used the more rapid evaporation of one solvent may cause the solid matter to precipitate



*Courtesy Modern Plastics*

FIG. 2.—Storage Tank for Phenolic Resin Used in High-gloss Varnishes.

in the remaining liquid. Also, the rapid evaporation of a solvent may cause cooling, resulting in the condensation of moisture on the film and a subsequent clouding effect.

3. Adsorption of liquids into the pores of a dry film. If the liquid adsorbed possesses nearly the same refractive index as the film a translucent film will be produced. If the refractive index varies widely from that of the film, opacity results. It should be noted however that the mere whitening of a film does not prove that the protective power has been lost.

A study on the tackiness of films from resin solutions has been made by Wolff.<sup>4</sup> It was concluded that tackiness is caused by the formation of colloidal

<sup>3</sup> W. H. Gardner, *Ind. Eng. Chem.*, 1931, 23, 1402.

<sup>4</sup> H. Wolff, *Farben-Ztg.*, 1920, 25, 668; 1922, 27, 2086; *Chem. Abs.*, 1920, 14, 2092; 1922, 16, 2610. H. Wolff and C. Dorn, *ibid.*, 1922, 28, 31; *Chem. Abs.*, 1923, 17, 216.

gels consisting of resin and residual solvent. To overcome this difficulty Wolff suggested either:

(1) The use of as large a proportion as possible of a single solvent in which the resin is very soluble;

(2) The incorporation of an additional solvent of suitable evaporation rate to slacken the fractional evaporation of solvents; or,

(3) The selection of such a combination of solvents that the least volatile is the best solvent.

Another problem in the study of solvents for varnishes and lacquers is to find those which will give the proper viscosity to the liquid being applied and at the same time will dissolve enough film-forming material so that only the minimum number of coatings will be necessary.<sup>6</sup> The cost of the solvents must be kept in mind, also, as was stressed previously. It might be mentioned that the odor and toxicity of solvents must be considered when the coating compositions are to be used on a small scale.<sup>6</sup> In large-scale operations, however, such properties are of minor importance if the solvents are cheap enough, since suitable means can be provided for eliminating dangerous or objectionable odors (e.g., conveniently placed vents for withdrawing the vapors).

The advent of cellulose lacquers and then the development of new synthetic resins (particularly the alkyd resins, Chapters 41-49) have been the cause of considerable rivalry in the coating field. As was mentioned before, the oil varnishes in most cases give desirable coatings but possess the disadvantages of slow drying and of poor weather-resistance. Consequently the perfection of low-viscosity nitrocellulose and cellulose acetate solutions was welcomed because it meant that quick-drying, moisture-resistant films were available. The lack of proper adhesion and flexibility in the early cellulose ester coatings as well as poor resistance to light hindered the full development of their use and paved the way for synthetic resins which would yield rapid-drying solutions and at the same time give films with the proper gloss, durability, adhesion and weather-resistance.<sup>7</sup> Advantages which have been pointed out<sup>8</sup> for the synthetic resin solutions include fast drying, excellent appearance, high hiding power, good adhesion, great resistance to light and to weather conditions and ease of application. The covering power, adhesion and resistance to light are qualities which make these finishes superior to the cellulosic lacquers.

Although one object in the manufacture of synthetic resins has been to replace or improve upon natural resins in coating compositions, another and undoubtedly greater development has been the making of plastic materials. The advantages of plastics have been emphasized repeatedly and are only too obvious. A plastic material has far greater adaptability than wood, metal or glass for the forming of articles of furniture, structural material and the like, provided that sufficient

<sup>6</sup> See Carleton Ellis, *Ind. Eng. Chem.*, 1933, 25, 125. D. B. Keyes, *ibid.*, 1925, 17, 558.

<sup>7</sup> See V. E. Yarsley, *Synth. and Applied Finishes*, 1933, 3, 80, 127, 172. 1933, 4, 21.

<sup>8</sup> For general articles on coatings involving synthetic resins see Carleton Ellis, *Ind. Eng. Chem.*, 1933, 25, 125. M. Bottler, *Kunststoffe*, 1927, 17, 149; *Chem. Abs.*, 1927, 21, 3137. H. Chase, *Synth. and Applied Finishes*, 1933, 4, 11. B. S. Covell, *Plastic Products*, 1933, 9, 56, 137. P. H. Faucett, *Paint, Oil, Chem. Rev.*, 1934, 96 (12), 22; *Chem. Abs.*, 1934, 28, 5280. C. E. Fawkes, *Paint, Oil, Chem. Rev.*, 1931, 91 (23), 13; *Chem. Abs.*, 1931, 25, 3853. E. Fonrobert, *Farben-Ztg.*, 1934, 29, 548; *Chem. Abs.*, 1934, 28, 5690; *Verfkronek*, 1934, 7, 333; *Brit. Chem. Abs. B*, 1935, 161. A. Foulon, *Parbe u. Lack*, 1933, 358, 380, 390; *Chem. Abs.*, 1933, 27, 5558. H. A. Gardner, *Circ., U. S. Paint Mfrs. Assoc.*, 1926, 261, 275; *Chem. Abs.*, 1926, 20, 2756. G. Genin, *Rev. gen. mat. plastiques*, 1932, 8, 195; *Chem. Abs.*, 1932, 26, 4485. J. Geschelin, *Automotive Ind.*, 1931, 65, 950; *Chem. Abs.*, 1932, 26, 3390. L. A. Jordan, *Synth. and Applied Finishes*, 1933, 4, 163. E. C. B. Kirsopp, *Am. Paint J.*, 1932, 16 (27), 54f; (28) 54f; *Chem. Abs.*, 1932, 26, 3123. H. H. Morgan, *Times Trade and Eng. Suppl.*, 1931, 28, (664), 10; *Chem. Abs.*, 1931, 25, 2862; *J. Oil, Col. Chem. Assoc.*, 1932, 15, 106; *Brit. Chem. Abs. B*, 1932, 562. H. G. Rains, *Oil, Col. Trades J.*, 1933, 83, 583; *Chem. Abs.*, 1933, 27, 4940. A. F. Suter, *ibid.*, 1934, 85, 606. M. G. Verheer, *Verfkronek*, 1930, 3 (1), 13; *Chem. Abs.*, 1930, 24, 3660. S. Werthan, *Paint, Varnish Prod. Mgr.*, 1931, 6 (4), 10; *Chem. Abs.*, 1932, 26, 2068. A short review of the history of paints and varnishes in America is given by G. B. Heckel, *J. Chem. Ed.*, 1934, 11, 487.

<sup>9</sup> "J. G.," *Peintures, pigments, vernis*, 1934, 11, 203.

strength can be imparted to it and, more important, that the material can be produced cheaply enough.

In order to form a perfect molding material a synthetic resin must meet a number of requirements. The most fundamental of these is that the resin can be easily molded or cast. Of course its melting point or softening point must be sufficiently high so that the molded article will keep its shape under the conditions in which it is used. A desirable quality in this connection is that the material will become infusible during the molding operation. This is exhibited notably in the urea-formaldehyde and phenol-formaldehyde resins.

Not only must the material mold easily but in the molding operation the resin should not stick in the mold since this involves loss of time and material.



*Courtesy Catalin Corp.*

FIG. 3.—Molding a Phenol-formaldehyde Resin. Molds Are Made of Lead.

The molded article should be capable of reproducing the high polish of the mold so that very little work is necessary on the finished article before it is ready for marketing. It should be noted here that if the resin has any chemical action on the metal of the mold, staining will result and as a consequence the finished article will be poorly made.

Not only should molded articles show a high polish but they should possess attractive colors. There is a great demand for light colors in synthetic resins because of the beauty which can thereby be imparted to molded articles. Hence the investigator in synthetic resins attempts to produce colorless or light-colored resins.\* This does not mean, however, that new dark-colored resins will be valueless, since they may possess other properties which outweigh the disadvantage of the dark color. For instance, if the resin is thermosetting, it can be used in moldings in which the primary requirement is strength and hardness, and color is of minor significance.

The electrical resistance and dielectric strength of synthetic resins is of im-

\* For a review on light-colored resins see C. W. Rivise, *Plastics*, 1929, 5, 189, 211, 254, 266, 317; *Chem. Abs.*, 1929, 23, 5600.

portance since the great development in the use of electrical apparatus and appliances of all kinds has created demands for an insulating material which can be formed into almost any shape conceivable and at the same time possess sufficient mechanical strength to make its use feasible.<sup>10</sup>

The chemical inertness of a synthetic resin has a great deal to do with its commercial success. It should at least not become stained or spotted by hot or cold water and should resist the action of mild acids and alkalies. In addition it should be immune to the action of some of the common organic solvents. It may seem paradoxical to expect a synthetic resin to dissolve in cheap organic solvents to form a varnish and at the same time expect a finished surface or a molded article of the resin to resist the action of these same solvents. What is meant is that the resin should be initially soluble in these solvents to form the varnish and at the same time should be capable of conversion into an insoluble form either by baking or by mere exposure to the oxygen of the air. Chemical inertness, fire-resistance and absence of odor help very much in promoting the use of synthetic resins in place of other materials.

Most important of all is the cost of a synthetic resin. Before any extensive replacement of wood or metal by molded or laminated products can be brought about, it is necessary to reduce production and fabrication costs to a minimum. This is of course accomplished by continued efforts to reduce the costs of raw materials and to improve the methods of resin manufacture and molding.

In discussing the properties desired in a synthetic resin it is well to present the characteristics of a few of the natural resins which have been found quite satisfactory, though not entirely perfect. Among the natural resins shellac possesses a good number of qualities desired in a synthetic resin. Shellac stands out from the other natural resins both in its origin and in its properties.<sup>11</sup> Whereas the other natural resins are strictly of vegetable origin, shellac occurs as a secretion from multitudes of lac insects feeding on certain types of hardwood or semi-hardwood trees. The resin is obtained principally from India, and in small quantities from Indo-China and Siam. For the most part shellac is cultivated; that is, the insects are placed on trees selected for the purpose. The insects suck sap from the host tree and exude resinous matter in which they become imbedded. Most of the resin is secreted by female insects since they outnumber the male of the species. The insects undergo two or three life-cycles a year, a new brood being produced during the process of resin-formation, and the parent insects dying in the secreted resin.

The shellac is harvested by breaking off the small branches incrustated with resin and then subjecting them to a crushing and winnowing operation to remove wood and bark. The material remaining, known as sticklac, consists of about 80 per cent resin contaminated with woody matter, wax and water-soluble constituents, principally a red dye, albumin and secreted sugars. The sticklac is broken into small pieces and washed to remove water-soluble material and woody particles. The cleaned resin, dried to about 2 per cent moisture, is known as seed-lac, in which form a great deal is exported.

In the process of making flaked shellac the material is subjected to what is essentially a filtering or straining operation to remove most of the dirt. The

<sup>10</sup> See H. Chase, *Plastics and Molded Products*, 1932, 8, 153. W. D. Owen and A. M. Thomas, *J. Oil, Col. Chem. Assoc.*, 1931, 14, 290; *Brit. Chem. Abs. B*, 1931, 1104. E. A. Bevan, E. N. Strathford and E. E. Walker, *Trans. Inst. Rubber Industry*, 1931, 6, 394; *Chem. Abs.*, 1931, 25, 4722; *J.S.C.I.*, 1931, 50, 134. With reference to insulating-varnishes see H. C. P. Weber, *Ind. Eng. Chem.*, 1925, 17, 11 and C. O. Harvey, *J.S.C.I.*, 1926, 45, 233.

<sup>11</sup> For general reviews on the preparation and uses of shellac see W. H. Gardner, *Ind. Eng. Chem.*, 1933, 25, 560. B. H. Knight, *The Chemist*, 1934, 11, 155. I. Mellan, *Chem. Industries*, 1934, 35, 315. A. F. Suter, *Brit. Plastics*, 1930, 2, 77.

seed-lac is placed in a long, narrow fabric bag and heated over an open-hearth charcoal fire. The ends of the bag are twisted so that the lac is extruded through the cloth<sup>12</sup> and drops onto a smooth hearth in irregular shapes which can later be worked into thin sheets, and, when cold, broken into flakes to form the ordinary shellac of commerce.<sup>13</sup> The principal uses for shellac have been in spirit varnishes, adhesives, fabric impregnation and moldings.<sup>14</sup>

For use in coatings, shellac has proved to be practically the best natural spirit-soluble resin. It forms films which are peculiarly tough and elastic and very resistant to abrasion. These properties can be demonstrated by attempting to grind a few flakes of orange shellac in a mortar. Not only is it difficult to reduce the flakes to a powder, but also the elasticity of the flakes causes them to fly out of the mortar. One disadvantage encountered with shellac films, however, is that they become stained and spotted by water and gradually lose their luster.<sup>15</sup> This has not been a serious drawback because the effect is not entirely permanent and because the hardness and toughness and quick-drying qualities of shellac varnishes far outweigh this slight fault.<sup>16</sup> The tough quality of shellac is a property to be sought for in synthetic resins intended for coatings.<sup>17</sup>

The thermoplastic character of shellac led to its extensive use in molding, principally in the production of insulating materials<sup>18</sup> and phonograph records.<sup>19</sup> The fact that it has a low coefficient of expansion enables shellac to be used for objects which must follow faithfully the intricate details of a mold. The low melting point of shellac is one drawback associated with its use, since moldings exposed to warm temperatures are apt to become distorted.

It is true that shellac polymerizes to an infusible product under the influence of heat<sup>20</sup> but the process is so slow that the heat-setting of the resin is not prac-

<sup>12</sup> The residue remaining in the cloth bag is known as "Kiri." The resin contained in this by-product has been used in cheap moldings. See S. Ranganathan and R. W. Aldis, *Brit. Plastics*, 1934, 6, 148.

<sup>13</sup> The estimated yearly production of shellac is 32,000 tons. A. J. Gibson, *J. S. C. I.*, 1933, 52, (May 19), 88. Of this the United States consumes 40, Great Britain 25 and all other countries 35 per cent. The distribution of uses is said to be: Phonograph records, 40 per cent, Varnishes and Electrical Insulation, 40 per cent; Hat- and Fabric-Stuffing, 10 per cent, Sealing Wax, Pyrotechnics, etc., 10 per cent.

<sup>14</sup> The chemical composition of shellac is considered in Chapter 50. For a method of determining insoluble matter, wax and ash in shellac see O. M. Olsen, *Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 47. See also W. H. Gardner, *Chem. Met. Eng.*, 1933, 40, 144. The solubility of shellac in various organic solvents is discussed by W. H. Gardner and W. F. Whitmore, *Ind. Eng. Chem.*, 1929, 21, 226. W. H. Gardner and H. J. Harris, *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 400. See also M. Rangaswami and M. Venugopalan, *Indian Lac. Res. Bull.*, 1928, 1; 1929, 2; *Chem. Abs.*, 1929, 23, 5050; 1930, 24, 3660. Compatibility of shellac varnishes with nitrocellulose has been studied by W. H. Gardner and B. Gross, *Ind. Eng. Chem.*, 1935, 27, 168.

<sup>15</sup> See M. Venugopalan and M. Rangaswami, *Ind. Eng. Chem.*, 1930, 22, 911. W. H. Gardner, *ibid.*, 1931, 23, 1402. According to J. W. Paisley (*ibid.*, 1932, 24, 163), the addition of up to 10 per cent of tricresyl phosphate to shellac increases the moisture-resistance. See, however, Hutter, *Farbe u. Lack*, 1932, 547, 556; *Chem. Abs.*, 1933, 27, 624. M. Rangaswami and R. W. Aldis, *Indian Lac. Res. Inst. Res. Note*, 1933, 9; *Chem. Abs.*, 1934, 28, 2202.

<sup>16</sup> It has been found that increased water-resistance, hardness and flexibility are imparted to shellac films by a baking operation in which the temperature rises from 60° to 140°C in 1.5-2 hours. These properties are likewise improved by the addition of sulphur or sulphur chloride to the shellac varnish. See M. Rangaswami and R. W. Aldis, *Indian Lac. Res. Inst. Res. Note*, 1933, 4; *Brit. Chem. Abs.*, B, 1933, 316. M. Venugopalan, *ibid.*, 1933, 10, 12; *Brit. Chem. Abs.*, B, 1934, 370. R. W. Aldis, *ibid.*, 1934, 18; *Chem. Abs.*, 1935, 29, 946. Water-resistance is improved also by incorporating 2-3 per cent of urea or thiourea. M. Venugopalan, S. Ranganathan and R. W. Aldis, *Synth. and Applied Finishes*, 1934, 5, 161.

<sup>17</sup> The possibility of applying shellac coatings by electrodeposition from alkali carbonate solutions is discussed by N. Narasimhamurthy and M. Sreenivasaya, *Ind. Eng. Chem.*, 1934, 26, 882.

<sup>18</sup> See W. H. Nuttall, *J.S.C.I.*, 1928, 47, 1367.

<sup>19</sup> For a general discussion on materials and methods in the manufacture of phonograph records see H. C. Bryson, *Brit. Plastics*, 1931, 3, 104, 160, 223, 259; 1932, 4, 48, 206; *J.S.C.I.*, 1933, 52, 495. See also R. Jones, *Brit. Plastics*, 1932, 3, 857.

<sup>20</sup> See, for instance, Swiss P. 95,239, 1923, to Mantle Lamp Co. of America; *Kunstst.*, 1923, 13, 31. See also A. F. Suter, *Brit. Plastics*, 1930, 2, 77 and W. Nagel and E. Baumann, *Wiss. Veröffentlich. Siemens Konzern*, 1932, 11, 99; *Chem. Abs.*, 1933, 27, 856; *Brit. Plastics*, 1932, 4, 250. Considerable study has been made on rendering polymerized shellac soluble. See R. W. Aldis, *Indian Lac. Res. Inst. Res. Note*, 1933, 7, 11; *Chem. Abs.*, 1933, 27, 3092; *Brit. Chem. Abs.*, B, 1934, 370. M. Venugopalan and R. W. Aldis, *ibid.*, 1934, 17; *Chem. Abs.*, 1935, 29, 946. M. Rangaswami and R. W. Aldis, *Indian Lac. Res. Inst. Bull.*, 1934, 19; *Chem. Abs.*, 1936, 29, 946.



ticable in good molding technic.<sup>21</sup> Therefore, in making molded articles from shellac and fillers the mixture is treated as a thermoplastic rather than a thermosetting material.<sup>22</sup> It is quite evident why the search is continually being made for plastic materials which will harden very rapidly when subjected to the pressures and temperatures used in molding.<sup>23</sup>

In addition to shellac, another natural product exhibits many desirable properties which should be possessed by synthetic resins. This is the material known as Japanese lac, which occurs as the sap in the Oriental tree, *Rhus verniciifera*.<sup>24</sup> The coating produced by this material is noteworthy for its hardness, luster and durability. In the opinion of Morgan<sup>25</sup> the type of resin towards which investi-



Courtesy Catalin Corp.

FIG. 4.—Removing Finished Product from Lead Molds Shown in Fig. 3.

gators should strive is a product of this nature which preferably could be applied in the liquid condition at ordinary temperature without the use of a volatile solvent.<sup>26</sup>

Another method of approach in the development of new resins is to modify natural resins so that they will be more adequately suited for the uses intended for

<sup>21</sup> S. Ranganathan and R. W. Aldis (*Indian Lac. Res. Inst., Res. Note*, 1933, 14; *Brit. Chem. Abs.*, B, 1933, 719) state that conversion of shellac to a tough mass requires 8 minutes at 220°C. and 127 minutes at 120°C., increase in pressure delaying the reaction. Urea, hexamethylenetetramine and mineral and polycarboxylic acids (e.g., hydrochloric, oxalic) accelerate the change. By preheating shellac at 110°C. before molding, the heat-stability of finished specimens is said to be improved. S. Ranganathan and R. W. Aldis, *ibid.*, 1933, 13; *Chem. Abs.*, 1934, 28, 3918.

<sup>22</sup> Methods of molding shellac are described in Chapter 68.

<sup>23</sup> Ordinary shellac contains 75-80 per cent of ether-insoluble resin, termed "pure lac resin." It is stated that this resin has a quicker rate of thermohardening and greater water-resistance than ordinary shellac. L. C. Verman and R. Bhattacharya, *Tech. Paper, London Shellac Res. Bur.*, 1934, 1. L. C. Verman, *J.S.C.I.*, 1935, 54, 86T.

<sup>24</sup> See K. Miyama, *J. Coll. Eng. Imp. University, Tokyo*, 1908, 4, 89, 201; *J.S.C.I.*, 1908, 27, 456; 1909, 28, 318. H. Pudor, *Z. offentl. Chem.*, 1910, 16, 315, *J.S.C.I.*, 1910, 29, 1119. Anon., *Bull. Imp. Inst.*, 1910, 8, 22; *J.S.C.I.*, 1910, 29, 639.

<sup>25</sup> H. H. Morgan, *Appl. Chem. Reports, Soc. Chem. Ind.*, 1921, 6, 346.

<sup>26</sup> For investigations on the constitution of Japanese lacquer see R. Majima and S. Cho, *Ber.*, 1907, 40, 4390. R. Majima and J. Tahara, *Ber.*, 1915, 48, 1606. R. Majima and G. Takayama, *Ber.*, 1920, 53, 1907. R. Majima, *Ber.*, 1909, 42, 1418; 1922, 55, 172, 191; *J. Tokyo Chem. Soc.*, 1919, 40, 91; *Chem. Abs.*, 1919, 13, 2862.

them. Thus has come about the production of ester gum and chlorinated rubber.<sup>27</sup> These can be considered "semi-synthetic resins" since they do not exactly fit into the class of synthetic resins nor are they truly natural materials since their properties have been modified.

Because of its acid nature, and consequent lack of resistance to moisture, rosin was once a greatly despised member of the natural-resin group. Reduction of of the acidity through esterification with glycerol to form ester gum helped a good deal in promoting the use of rosin in varnishes. A greater move was the discovery that excellent varnishes are formed from rosin and tung oil. Although the fossil resins were not entirely compatible with tung oil, rosin was found to have exceptional merit in this respect. In addition rosin prevents the gelatinization of tung oil at the temperatures used in preparing varnish. At the same time the tung oil gives sufficient waterproofness to the varnish, so that the two raw materials are mutually beneficial.<sup>28</sup> Ester gum is likewise compatible with tung oil, giving even better results. Consequently the modification of a once-despised natural resin has placed it in the ranks of the most useful resins.

The chapters which follow present a great number of attempts to produce synthetic materials to meet the demand for new and better coatings and improved molded articles. It should be borne in mind that relatively few of these have been really successful and that as a consequence the search still continues both for resins with improved qualities and for new uses for those resins already developed. As the public becomes more and more "synthetic-resin conscious" the number of resins and the diversity of their uses increase.

<sup>27</sup> Modified rosin and other resins are treated in Chapters 37-39. Chlorinated rubber is discussed in Chapter 55.

<sup>28</sup> R. L. Houck, *Paint, Oil, Chem. Rev.*, 1928, 86, (21), 10; *Chem. Abs.*, 1929, 21, 5336, has suggested there may be a reaction between the acid resin and the tung oil to form mixed esters so that the varnish film in this case may be regarded as a synthetic resin.

## Chapter 3

### The Resinous State

The nature of solids and liquids is perplexing and complicated save in idealized cases. Between the solid and the liquid there are a number of transitions which are of a puzzling character. A great number of names has been used to distinguish these intermediary states. They have been called gels, glasses and also vitreous, plastic, colloidal, mesomorphic and amorphous states. By considering matter as being divided into two classes,<sup>1</sup> it is possible to avoid some of the ambiguity. In the crystalline state, matter is arranged in a definite order according to the laws of lattice structure. In the amorphous state, matter is in complete disorder.

When a solid material is dissolved in a volatile solvent and the solvent allowed to evaporate, three very distinct phenomena may take place: (1) the solvent on evaporating deposits crystals; (2) the solid may precipitate as an amorphous mass; or (3) no solid separates but the solution becomes more viscous, yielding the solid as a vitreous or glassy mass. In the first instance there is such a directing force between the molecules that at the point of crystallization the molecules become arranged in a lattice structure and solidification takes place rapidly. In the formation of amorphous materials, however, the attraction forces do not necessarily disappear but no one force predominates and no regular lattice can be formed.

The formation of a glassy mass can be observed not only when a solid is dissolved in a liquid but also in the case of a pure substance. If a pure molten compound is cooled below its melting point, the melt begins to crystallize at one or at several points. At a certain temperature, i.e., a few degrees below the melting point, it is almost impossible to prevent the tendency to crystallization. If one quickly passes through this range of temperature, the tendency toward crystallization vanishes and the melt becomes viscous and solidifies to a glass.\*

Normally the glassy state is associated with transparent silicate glass, but an obvious extension is to such a material as vitreous arsenious oxide. The general physical characteristics of a glass are, however, shown by many brittle synthetic resins, and indeed lines of demarcation are exceedingly ill-defined.

The case of dextrose can serve as an illustration of a typical non-siliceous glass. Crystalline dextrose, when heated at 160°C. for 10-15 minutes and cooled to the ordinary temperature at a pressure of 4 atmospheres in nitrogen, forms a clear colorless material, which softens at 40° and forms a thick viscous liquid at 60°. The refractive index-temperature curve shows a change in slope over the interval 20-30°, i.e., at below the softening point.\* Other glassy materials of a similar nature (e.g., from glycerol-glucose, propylene glycol-glycerol-glucose) have been prepared.\* Reference may be made in this connection to the remarkable adhesive properties of overheated glycollic acid. By heating glycollic acid

<sup>1</sup> This classification is due to M. Polanyi, *Umschau*, 1930, 34, 1001; *Chem. Abs.*, 1931, 25, 1132.

\* For application of this phenomena to mineral oils to account for variation of melting points accompanying the change of state, see P. Woog, E. Ganster and F. Coulon, *Compt. rend.*, 1931, 193, 850; *Chem. Abs.*, 1932, 26, 1424.

<sup>2</sup> G. S. Parks, H. M. Huffman and R. F. Cattoir, *J. Phy. Chem.*, 1928, 32, 1366.

<sup>3</sup> G. S. Parks, S. B. Thomas and W. A. Bilkey, *J. Phy. Chem.*, 1930, 34, 2028; *Chem. Abs.*, 1930, 24, 5210.

gradually to 150°C. and maintaining the temperature at this point for several hours and cooling a hard compact product is formed with excellent properties as an adhesive. This material may well be a glass.<sup>5</sup> Fused sucrose octa-acetate is found also to have a glassy or resinous character, and its use as an ingredient of anhydrous adhesives, as a gum substitute of lacquers and as a plasticizer has been suggested.<sup>6</sup>

Berger<sup>7</sup> considers the formation of a glass from the liquid state as continuous process, taking place through the viscous (supercooled) state to the brittle state. Accordingly a break occurs in the property-temperature curve at the transition from the supercooled to the vitreous state. Brittle glass is, according to this conception, not merely a supercooled liquid, but represents a definite state of matter. According to a theory of the vitreous state developed by Rosenham<sup>8</sup> glass is considered as an assemblage of atoms in which certain molecular groupings may occur. Even in irregular assemblages of atoms, there are tendencies toward some aggregation even though most of the linkage bonds are unsatisfied. A small portion of the interatomic linkages is operative and the latent heat of fusion (representing the energy stored in unsaturated bonds) is largely retained in cooling and setting. This accounts for the low absorption of heat during melting and the little or unnoticeable evolution of heat on cooling which is a characteristic property of glasses. There is an intermediate stage between the elastic solid and the viscous liquid in which the rupture of bonds may occur for a time after the application of stress but with a storage of sufficient energy to arrest any further rupture. Morey,<sup>9</sup> on the other hand, on the basis of x-ray patterns considers that the distinguishing feature of the glassy state is a random, non-repeating atomic network.

Zachariasen<sup>10</sup> maintains that the atoms in glass are linked together by forces which are essentially that kind which exist in crystals. The mechanical properties of glass are directly comparable to those of crystals, in fact, the strength of glass may excel that of the corresponding crystalline form. In glass, however, the atoms oscillate around definite equilibrium positions over large ranges of temperature and even though one may consider a three-dimensional network in glasses as in crystals, the network is not periodical and symmetrical. The arrangement can not be entirely one of randomness, however, inasmuch as the internuclear distances do not sink below a given minimum value. The principal difference between the network in a crystal and that of glass is the symmetry and periodicity in the first instance and the absence of these properties in the latter. Each unit cell in a crystal must contain an integral number of stoichiometric molecules because all the unit cells are alike. In glass, however, the unit cell is infinitely larger. As in crystals the transparency of glasses can be explained on the basis of an extended network.

Very few of the known oxides readily produce a glass. Whereas silicon dioxide and boron trioxide form glasses, attempts with titanium oxide and aluminum oxide have not been so successful. Goldschmidt<sup>11</sup> has tried to correlate the ability to form glass with the value of the radius ratio  $R_a/R_0$  for the oxides  $A_mO_n$ . The radius ratio of the oxides which have been prepared in the vitreous form is about

<sup>5</sup> Report of Adhesives Research Committee; *Chem. Age (London)*, 1932, 27, 167.

<sup>6</sup> C. J. Cox and J. Metschl, *Ind. Eng. Chem. News Ed.*, 1932, 10, 149.

<sup>7</sup> E. Berger, *J. Amer. Ceram. Soc.*, 1932, 15, 647; *Chem. Abs.*, 1933, 27, 821.

<sup>8</sup> W. Rosenham, *J. Soc. Glass Tech.*, 1927, 11, 77; *Chem. Abs.*, 1928, 22, 1833. See P. Mondain-Monval, *Ann. chim.*, 1935, (11) 3, 5; *Chem. Abs.*, 1935, 29, 2042.

<sup>9</sup> G. W. Morey, *J. Amer. Ceram. Soc.*, 1934, 17, 315; *Brit. Chem. Abs. B*, 1935, 148.

<sup>10</sup> W. H. Zachariasen, *J.A.C.S.*, 1932, 54, 3841.

<sup>11</sup> V. M. Goldschmidt, "Geochemische Verteilungsgesetze der Elemente VIII," *Vid. Akad. Skr., Oslo*, 1926, (8), 137.

0.2-0.4. This arrangement corresponds to the tetrahedral arrangement of oxygen atoms around the atom *A*. Zachariassen derives a formula for the gross chemical composition of a glass to be  $A_mB_nO$  where *B* represents the cations, *A* represents other cations, *m* and *n* give the number of cations *A* and *B* per oxygen atom. It is concluded that a glass will have the most advantageous properties if *n* has a value of about 0.5. Cations *A* must carry a small charge and have a large radius. Hagg,<sup>12</sup> however, believes that large and irregular groups exist in melts. In the inorganic glasses the formation of these groups is due to the possibility of coördinating oxygen atoms in a definite way. If the number of available oxygen atoms is less than necessary for the formation of polyhedral groups with the required coördination, the polyhedra are linked together sharing oxygen atoms. The resulting groups delay crystallization and thus cause the formation of glass.<sup>11</sup>

Tammann,<sup>14</sup> to whom much of our knowledge of glasses and supercooled liquids is due, has described an experiment which illustrates a similarity between a resin and a glass. The height of rebound of a steel ball from a rosin surface at temperatures between 20-70°C was measured. An almost constant rebound was observed between 20-50°, and then there was a sharp decrease to no rebound at 70°. Somewhere in this temperature range rosin lost its brittleness, just as a glass does, though it showed no sign of softening.<sup>15</sup> In this respect rosin behaved as a typical glass. The hardness of the surface of glass, as measured by the pressure needed to cause initial rupture of the surface, diminishes continuously over the softening range, but this diminution commences before softening sets in. The hardness vanishes at the lowest temperature at which threads can be drawn from the glass.<sup>16</sup>

The kinetics of the transformation of the supercooled melt to the crystalline phase has been studied especially by Tammann.<sup>17</sup> In a supercooled liquid, the molecules do not tend rapidly to assume their positions in the space lattice of the crystal because crystallization would set in immediately below the melting point. Only a small portion of the molecules are properly oriented and these serve as nuclei or crystallization centers from which further crystallization takes place. In supercooled melts, those molecules possessing a low enough kinetic energy will stick together to form a minute crystal which acts as a nucleus. At lower temperatures, however, the production of nuclei becomes less favorable because of the decrease in molecular motion and the increase in viscosity. Both of these factors are unfavorable for the formation of nuclei.

There is considerable experimental evidence to indicate that one of the factors influencing crystallization is the treatment of the liquid previous to cooling. Othmer<sup>18</sup> observed a diminution in the tendency to crystallize with increased preheating of the liquid. No simple explanation can be offered to explain this behavior. Certain solutions can not be made to crystallize except by inoculating. Supersaturated solutions of sugar and tartaric acid remain stable.<sup>19</sup> On careful filtration through glass wool, supercooled melts of salol, thymol, benzophenone,

<sup>12</sup> G. Hagg, *J. Chem. Physics*, 1935, 3, 42; *Chem. Abs.*, 1935, 29, 1302

<sup>13</sup> For a consideration of glasses as a fourth state of matter, see E. Bräger, *Z. tech. Physik*, 1931, 12, 344; *Chem. Abs.*, 1931, 25, 5068. Also O. Koerner and H. Salmang, *Z. anorg. Chem.*, 1931, 199, 235; *Brit. Chem. Abs. A*, 1931, 220 and *Glashütte*, 1932, 52, 852; *Chem. Abs.*, 1933, 27, 821. H. Salmang, *Naturwissenschaft*, 1933, 21, 391; *Chem. Abs.*, 1933, 27, 4975. O. Koerner, H. Salmang and W. Lerch, *Sprechsaal*, 1932, 65, 925; *Chem. Abs.*, 1933, 27, 4975

<sup>14</sup> G. Tammann, *Glastech. Ber.*, 1930, 7, 445.

<sup>15</sup> See P. P. Kobeko and I. G. Nelidov, *Physik. Z. Sowjet union*, 1933, 4, 516, 680, 695, 703; *Chem. Abs.*, 1934, 28, 1234, 1235, for electrical conductivity and dielectric constants of substances in the softening interval.

<sup>16</sup> G. Tammann and R. Klein, *Z. anorg. Chem.*, 1930, 192, 161; *Brit. Chem. Abs. A*, 1930, 1358.

<sup>17</sup> G. Tammann, "Kristallisieren und Schmelzen," Leipzig, 1903.

<sup>18</sup> P. Othmer, *Z. anorg. Chem.*, 1915, 91, 209; *Chem. Abs.*, 1915, 9, 1866.

<sup>19</sup> A. Schweitzer, *Rec. trav. chim.*, 1933, 52, 678; *Brit. Chem. Abs. A*, 1933, 897.

o- and m-cresol, acetophenone and guaiacol have no tendency toward spontaneous crystallization.<sup>20</sup>

Although crystallization centers can not exist in a melt at temperatures above the melting point,<sup>21</sup> Richards<sup>22</sup> has suggested that the crystal form may persist above the melting point provided an adsorbent is present for which the heat of binding of the crystalline adsorbate is greater than the liquid adsorbate.

Haber<sup>23</sup> differentiated two distinct processes in the formation of the nuclei: one, the rate of aggregation and second, the rate of arrangement. The rate of aggregation corresponds to the coagulation velocity whereas the rate of arrangement is related to the formation of nuclei and of crystallization proper. The disparity between the rate of aggregation and that of arrangement determines whether the particle precipitates as crystalline or amorphous. When the rate of aggregation is large and that of arrangement is small, the particle will appear as amorphous, which may become crystalline after a long time. On the other hand, when the rate of arrangement is also large, no amorphous mass will be formed.

Von Weimarn<sup>24</sup> has developed an elaborate theory to account for crystallization and the supercooled state. Crystals may be divided into three classes: first are those crystals in which not any one of the three dimensions shows a marked development over the other two. These are termed "neutral" crystals. In the second class are those crystals in which one dimension is less developed than the other two. The third class takes in those crystals with one dimension highly developed; an example of this last class is to be found in the fibrous crystals.

In solution there exists around each crystal a vectorial field or vectorial atmosphere which prevents the crystals from approaching one another and which allows parallel orientation. Due to differences in concentration there will be diffusion currents but these again will be vectorial. Crystallization can therefore be looked upon as a "vectorial polymerization."

From a very extensive investigation on the form of precipitates, von Weimarn sums up his results in the following equations:

$$N = K \frac{P}{L}$$

where

$N$  is the number of crystallization centers,

$K$  is a factor involving viscosity,

$P$  is the degree of supersaturation and

$L$  is the solubility.

If  $K$  and  $P$  are small and  $L$  relatively large then the value for  $N$  will be small. The resulting precipitate will be in the form of a small number of large crystals. If  $K$  and  $P$  are large and  $L$  small, then  $N$  will be large and the precipitate will be in the form of a large number of very small crystals. Under these conditions the whole mass sets to a gel. In other words, when the solutions are very dilute, the solid separates as a crystalline form. At low concentration, the velocity with which nuclei are formed is very small and the crystals grow slowly in this weakly supersaturated solution. In concentrated solutions, however, jellies are formed inasmuch as at high concentration the rate of the formation of nuclei is very great and these nuclei form a felt-work without crystallization.<sup>25</sup> Low solubility and high molecular weight are properties

<sup>20</sup> J. Meyer and W. Pfaff, *Z. anorg. allgem. Chem.*, 1934, 217, 257; *Chem. Abstr.*, 1934, 28, 4653.

<sup>21</sup> See G. Tammann and H. E. von Gronow, *Z. anorg. allgem. Chem.*, 1931, 200, 57.

<sup>22</sup> T. W. Richards, *J.A.C.S.*, 1932, 54, 479.

<sup>23</sup> Haber, *Ber.*, 1922, 55, 1717.

<sup>24</sup> P. P. von Weimarn, "Theory of the Colloidal State of Matter" in J. Alexander, "Colloid Chemistry," New York, Chem. Cak. Co., 1926, I, 27. "Rubber-like and Liquid-crystalline States," *ibid.*, 1931, III, 90. See also P. P. von Weimarn and T. Hagwara, *Kolloidchem. Beihefte*, 1927, 23, 400; *Chem. Abstr.*, 1927, 21, 3293.

<sup>25</sup> P. P. von Weimarn has shown that one can obtain any anhydrous salt in a gelatinous form by precipitating under conditions where the supersaturation is enormous. By mixing concentrated solutions of manganous sulphate and barium sulphocyanate a gelatinous precipitate of barium sulphate comes

which are associated with gels. Conditions which bring about supersaturation, such as rapid cooling or slow mixing, also favor gelation.

In crystals of ultramicroscopic size, the vectorial fields will be liquid and the whole aggregate will appear either liquid or semi-liquid. At no time, however, does crystallinity cease to exist and crystals can be macro-, micro- or ultramicro-crystalline. The amorphous state arises more through the limits of microscopic resolution than through any differences in structure.

Moreover when crystals become sufficiently disaggregated mechanically, materials are obtained which, though solid, can not be distinguished from liquids. A supercooled melt, therefore, is considered to be identical with that produced mechanically.

### PLASTICITY

Plasticity as well as viscosity both imply the meaning to flow but it is generally conceded that soft solids do not behave in the same manner as viscous liquids. Because of the overlapping of solids and liquids, differences in interpretation arise and no one definition can satisfactorily account for all of the conflicting phenomena. One of the most satisfactory definitions is as follows: plasticity is the susceptibility to and the retention of deformation.<sup>26</sup> In contrast, a brittle body under mechanical stress loses its coherence. An elastic body, on the other hand, though easily deformed, readily assumes its original shape.

Several factors are involved, however, in the susceptibility to deformation. Both wax and sealing wax are brittle if the pressure is applied rapidly; they can be considered plastic if the rate of deformation is slow. Glass under the same conditions can be considered as plastic at ordinary temperatures. Under high temperatures, it behaves as a deformable liquid which retains its shape by rapid cooling. Spring<sup>27</sup> reported that under sufficiently high pressures, solids behaved like mobile liquids; this apparent fluidity only occurs when there is a shearing force together with pressure.<sup>28</sup>

Part of the anomaly in plasticity can be avoided by the use of the classification of Polanyi,<sup>29</sup> namely, that there are two forms of matter, crystalline and amorphous. In the ordered state are included metals and salts whereas in the amorphous state are such substances as glass, varnishes and the like. These substances differ markedly with respect to plasticity. When amorphous materials change their form, the molecules change places. Increasing the temperature causes an increase in the mobility of the molecules. The plasticity of amorphous substances, therefore, is greatly dependent on temperature. In crystalline substances, the plasticity even at high temperature (that is, below the melting point) changes but very little due to the fact that the molecules are bound and can not change places.<sup>30</sup>

Metals, however, do have a plasticity; this can be shown in the case of polycrystalline metals which can be forced through an orifice under pressure.<sup>31</sup> The plasticity depends upon the movements of the molecules over one another.<sup>32</sup>

Athermal plasticity arises in unicrystals (zinc and cadmium). They possess

down temporarily. Concentrated solutions of calcium chloride and ammonium carbonate yield gelatinous calcium carbonate. See "Grundzüge der Dispersoid Chemie," 1914.

<sup>26</sup> E. Karrer, *Ind. Eng. Chem.*, 1929, 21, 770.

<sup>27</sup> W. Spring, *Ann. chim. phys.*, 1881, (5) 22, 170; *J.C.S.*, 1881, 40, 498.

<sup>28</sup> Spiezza, *Atti. Acad. Sci. Torino*, 1911, 45, 525, 1912, 46, 682.

<sup>29</sup> M. Polanyi, *loc. cit.*

<sup>30</sup> H. Kotte, *Stahl u. Eisen*, 1930, 50, 1071; *Chem. Abs.*, 1931, 25, 4753.

<sup>31</sup> N. Kurnakow and S. Zhemchuzhnyi, *Z. anorg. Chem.*, 1909, 64, 149; *Chem. Abs.*, 1910, 4, 435.

<sup>32</sup> R. Becker, *Physik. Z.*, 1925, 26, 919; *Chem. Abs.*, 1926, 20, 3254.

a low elongation limit which at low temperatures becomes independent of loading velocity and temperature. It appears, therefore, that at absolute zero, deformation would occur under conditions not markedly different from that of room temperature.<sup>33</sup> In the thermally plastic substances (glass, pitch and shellac) where plasticity depends on heat motion, one would expect that at absolute zero the plasticity would disappear.<sup>34</sup>

Another type of plasticity occurs in which two phases enter, one the solid and the other liquid. Apart from such factors as fineness, softness, laminated structure and roughness of surface, one must consider the viscous layer between the particles and the surface reaction between the liquid and the solid phases.<sup>35</sup> This type of plasticity has been termed "colloidal" because the most important factor appears to be the development of an active surface.<sup>36</sup> Substances which are wetted by a suitable liquid (which will not dissolve the particle) will form plastic masses provided the material is sufficiently divided. Silica, tungstic oxide and red phosphorus will give good plastics with water alone. Other oxides (titanium, zirconium and thorium) gave no plasticity with water; with a strong acid solution in place of the water the plasticity improved markedly. A sufficiently great thickness of the liquid layer is important for obtaining strong plasticity.<sup>37</sup>

There is another phenomenon closely related to both the particle size and to loose packing and this is known as "thixotropy." A material is considered thixotropic which when at rest becomes solid but which liquefies again on agitation. This process of solidification and liquefaction can be repeated as often as desired. The phenomenon requires a sufficient thickness of liquid layers between the particles and also demands some sort of attractive forces between the solid particles. These same forces influence the consistency of plastic masses. Freundlich and Juliusberger<sup>38</sup> emphasize that plasticity and thixotropy exist when packing is not too close, where there is a large volume of sedimentation and where no Osborne Reynolds phenomenon enters.<sup>39</sup>

The importance of the particle shape in plastic masses was pointed out by Le Chatelier.<sup>40</sup> When the particles are of a decidedly non-spherical shape, they display characteristic streaks on stirring showing a persistent layering effect. Concentrated suspensions of quartz powder stirred in water reveal streaks of silky luster.<sup>41</sup>

Wiener<sup>42</sup> as a result of theoretical investigations showed that any substance which was intrinsically lamellar in structure would in sufficiently small layers

<sup>33</sup> See, however, F. Simon, *Z. anorg. allgem. Chem.*, 1931, 203, 219; *Chem. Abs.*, 1932, 26, 1840.

<sup>34</sup> M. Polanyi and E. Schmid, *Naturwiss.*, 1929, 17, 301; *Brit. Chem. Abs.*, A, 1929, 743. See also M. Polanyi and E. Schmid, *Mitt. deut. Materialprüfungsanstalt Sonderheft*, 1930, 10, 101; *Chem. Abs.*, 1931, 25, 5127.

<sup>35</sup> H. Salmang, *Z. anorg. Chem.*, 1927, 162, 115; *Brit. Chem. Abs.* B, 1927, 602.

<sup>36</sup> O. Ruff, *Z. anorg. Chem.*, 1924, 133, 187; *Chem. Abs.*, 1924, 18, 1396. See also *Z. anorg. allgem. Chem.*, 1928, 173, 373; *Chem. Abs.*, 1929, 23, 2005.

<sup>37</sup> Close packing is detrimental to plasticity. When moist fine powders are stirred they appear to become dry and hard; on standing they become moist again. This is known as the Osborne Reynolds's effect (*Phil. Mag.*, 1885, (5) 20, 469) and is due to close packing. When dislocated, the particles separate and the amount of water is not sufficient to fill the interstices. The mass under these conditions appears dry. During the settling the particles become closely packed again with enough water to fill the cavities and the particles appear moist. The Osborne Reynolds's effect is the exact opposite of thixotropy.

<sup>38</sup> H. Freundlich and F. Juliusberger, *Trans. Faraday Soc.*, 1934, 30, 333; *Chem. Abs.*, 1934, 28, 4286. See also A. Waele, *J. Rheol.*, 1931, 2, 141; *Chem. Abs.*, 1931, 25, 5818. E. L. McMillen, *ibid.* 1932, 3, 163, 179; *Chem. Abs.*, 1932, 26, 5243.

<sup>39</sup> See French P. 686,764, 1929, to K. D. P. Ltd., *Chem. Abs.*, 1931, 25, 845.

<sup>40</sup> H. Le Chatelier, "La plasticité de l'argile" in *Gedenboek aangeboden aan J. M. van Bemmelen* uitgegeven bij C. du Boor Te Helde, 1910, 163.

<sup>41</sup> H. Diesselhorst, H. Freundlich and W. Leonhardt, *Elster Gestel Festschrift*, 1915, 453; *Kolloid Z.*, 18, 26; *Chem. Abs.*, 1916, 10, 2662. See also H. Freundlich, "Colloid and Capillary Chemistry" E. P. Dutton, N. Y., 1922, 404.

<sup>42</sup> O. Wiener, *Ber. Süchs. Ges. Wiss. (Math. phys. Kl.)*, 1910, 62, 256; *Chem. Abs.*, 1912, 6, 951.



show the phenomenon of double refraction, the "rod double-refraction." A case of this type was early found in fibrous alumina.<sup>43</sup> Ambronn<sup>44</sup> investigated the simultaneous double refraction by rods and the specific double refraction. Rods of celloidin (nitrocellulose) and cellulose, when examined, showed that the celloidin had a negative sign whereas cellulose was positive. This appeared to Ambronn to be a confirmation of Nägeli's<sup>45</sup> theory of crystalline micellae.<sup>46</sup>

Particle size as well as shape likewise has a definite bearing. To form plastic masses there seems to be a distinct optimum in size which varies from 0.3-3 $\mu$ .<sup>47</sup> When the particle is too small, even the influence of the non-spherical shape, so necessary for cohesion, falls off rapidly. The smaller particles, moreover, have a stronger Brownian movement and this movement tends to make the mass less firm.

The particle size cannot be too large. The maximum diameter appears to be in the neighborhood of 10 $\mu$ .<sup>48</sup> Particles when too large become more closely packed thereby decreasing the amount of liquid between the layers, as well as decreasing the area of the interfacial surface. Both of these factors are detrimental to elasticity.

The effect of mechanical treatment, and especially that of the fineness of dispersion, on plastic properties is of prime importance in the case of certain synthetic resins, just as it is in the case of clays and similar systems. Manfred and Obrist<sup>49</sup> have discussed this phase of the problem for plastics made from casein. Casein itself is not inherently plastic.<sup>50</sup> When pulverized or finely ground casein is mixed with 15-45 parts of water, an immediate swelling of the casein particles sets in. The subsequent plastification is carried out either entirely by mechanical means, or by a combination of mechanical and chemical treatment. In the first case extrusion machines are used, resembling those employed in the rubber industry. The casein particles are gradually compressed; under these conditions their mutual interference and friction causes considerable disaggregation. When this change has proceeded to its full extent, the particles pass into a zone heated to 80-85°C., where they become welded together, forming a more or less homogeneous product.

On this basis, the process of forming a plastic material consists first of all in a disintegration of pre-existing aggregates. The re-aggregation to form a plastic substance occurs between rod-like particles, which set into chains. If the disaggregation is carried to a stage at which the rod-like particles themselves are broken down, the chain structures do not form so readily. The elastic properties of artificial and natural plastics, therefore, depend more on their condition of orientation, which is determined by the plasticizing treatment they receive prior to hardening or setting, than upon the initial chemical condensation.<sup>51</sup> This theory has been called the "principle of conformation by assemblage."<sup>52</sup>

Against such an extreme view there is much to be said. One very important fact which must not be overlooked is that resins, either natural or synthetic, are not composed of a single entity, but usually of several types of molecules. It may, indeed, be necessary for this condition to be fulfilled if a resin is to form.

<sup>43</sup> H. Ambronn, *Kolloid. Z.*, 1910, 6, 222.

<sup>44</sup> H. Ambronn, *Kolloid. Z.*, 1916, 18, 90, 273; *Chem. Abs.*, 1917, 11, 1357, 2298.

<sup>45</sup> K. von Nägeli, "Pflanzenphysiologischen Untersuchungen," Zurich, 1858.

<sup>46</sup> H. Ambronn, *Nachr. Kgl. Ges. Göttingen, Mathem. Phys.*, 1919, 229, *Chem. Abs.*, 1921, 15, 3393. For the correctness of this assumption see Chapter 4.

<sup>47</sup> O. Ruff and A. Riebeth, *Z. anorg. allgem. Chem.*, 1928, 173, 373; *Chem. Abs.*, 1929, 23, 2005.

<sup>48</sup> H. Salmang, *loc. cit.*

<sup>49</sup> O. Manfred and J. Obrist, *Kolloid. Z.*, 1927, 41, 348; *Chem. Abs.*, 1927, 21, 2535; *Plastics*, 1928, 31.

<sup>50</sup> See F. L. Browne, "Technologically Useful Properties of Casein" in J. Alexander, "Colloid Chemistry," Chem. Cat. Co., N. Y., 1932, IV, 399.

<sup>51</sup> O. Manfred and J. Obrist, *Kolloid. Z.*, 1927, 42, 174; *Chem. Abs.*, 1927, 21, 2991. See also *Kolloid Z.*, 1927, 43, 41; *Chem. Abs.*, 1928, 22, 173.

<sup>52</sup> O. Manfred and J. Obrist, *Rev. gen. mat. plast.*, 1929, 5, 195, 251; *Chem. Abs.*, 1929, 23, 4682.

In addition to this, specific chemical effects do undoubtedly enter into resin formation, though in a number of well-known instances it is the long rod-like molecules which form resins.

**Measurement of Plasticity.** Bingham<sup>22</sup> defined plasticity in terms of two independent factors. Under a small shearing stress, the solid would permanently hold its shape. Under a larger shearing stress, the solid could readily be deformed, worked or molded. In the case of a viscous fluid, a linear relation exists between the volume of flow and the rate of shearing stress. Plastic solids behave differently in that a definite amount of the shearing force is used up in overcoming the internal friction of the material. When the rate of stress is just equal to the yield value, that is, the point at which the plastic solid responds to the shearing stress, then the material is said to have reached its elastic limit. Increase in the stress beyond the elastic limit results in plastic flow.

Karrer<sup>24</sup> has suggested the following quantitative definition of plasticity:

a substance has unit plasticity which deforms a definite amount under some standard conditions when a force of 1 kg. per sq. cm. acts on it for 1 second, and the whole of this deformation is permanently retained. The name "pla" was suggested for the unit which could be measured in a plastometer. A sample of the substance to be measured is cut in the form of a small cylinder 1 cm. long and 1 cm. in diameter and is placed between two jaws of the same diameter as the sample; the upper jaw being movable in a vertical direction. A spring is then released, which causes the upper jaw to move down, imparting to the sample a deformation which depends upon its softness.

The amount of deformation is recorded on a dial. The pressure is released after a definite time (e.g., 1 second), and the amount of recovery in, say, 5 seconds, is also recorded automatically. The plasticity is then defined by

$$P = C \frac{D}{F}$$

where  $C$  is a constant,  $D$  is the deformation retained (expressed as a percentage of the initial length) and  $F$  is the deforming force.  $F$ , therefore, is a function of the hardness of the material, whereas  $D$  is governed by the permanent set.

Karrer has also developed expressions for the retentivity of the material and for its softness, some typical relative values can be seen in Table 2.

TABLE 2.—*Plasticity of Certain Materials.\**

Material	Temp.	Softness	Retentivity	Plasticity
Chewing gum				
Unmasticated . . . . .	20° C.	0.342	0.722	243
Masticated 15 times . . . . .	20°	0.284	0.843	2410
Masticated 30 times . . . . .	20°	0.256	0.814	2070
Beeswax . . . . .	20°	0.0545	0.25	13.6
Asphalt . . . . .	20°	0.0211	0.20	4.22
Cast steel . . . . .	20°	0.000121	0.0278	0.00034
Crude rubber . . . . .	30°	1.16	0.0748	8.73
Smoked sheet . . . . .	100°	1.66	0.0345	50.7
Unmasticated . . . . .	140°	2.02	0.0692	139.9

\* E. Karrer, *Ind. Eng. Chem.*, 1929, 21, 770.

These figures give a general idea of the differences which arise in materials, all of which have some claim to be considered as plastic. Definition of temperature will also be necessary in defining plasticity, since for a great number of synthetic resins there is a large temperature coefficient.

Williamson<sup>25</sup> has pointed out that many dispersions do not exhibit a real yield

<sup>22</sup> E. C. Bingham, "Fluidity and Plasticity," McGraw-Hill, N. Y., 1922, 216 ff. See also J. Alexander, "Colloid Chemistry," I, 720.

<sup>24</sup> E. Karrer, *Ind. Eng. Chem.*, 1929, 21, 770; *ibid. Anal. Ed.*, 1929, 1, 158; 1930, 2, 96.

<sup>25</sup> R. V. Williamson, *Ind. Eng. Chem.*, 1929, 21, 1108.

value and cannot be molded, yet their flowing properties resemble in some respects those of ideal plastics. Such dispersions are called pseudo-plastics. de Waele<sup>55</sup> gives as examples of this type of system cellulose nitrate sols, gelling gelatin sols and some liquid-liquid emulsions. True plastic systems resemble those which are pseudo-plastic, at a rate of shear which is above a certain critical value. The rigidity component manifests itself at low values of shear, but disappears progressively as the rate of shear is increased. The difference between the two states, then, appears to depend fundamentally on the lower rigidity of the pseudo-plastic state.

Bingham and Green<sup>57</sup> have shown that paints do not flow in accordance with the law of viscous flow but show certain properties of plastic flow. This failure of yield value and mobility constants in the equation of flow, Williamson, Patterson and Hunt<sup>58</sup> took as a measure of the brushing and flowing properties of paints. The method was based upon the manner in which the apparent fluidity varies with shear at low rates of shear in a modified Stormer<sup>59</sup> viscosimeter. McMillen,<sup>60</sup> however, showed that this instrument does not allow accurate measurement of apparent fluidity in leveling, due to friction. The method was, in effect, one of extrapolation.

A paint or an enamel is plastic in the sense that a certain amount of force is necessary to change its shape. The necessary force is termed yield value. One substance which lowers the yield value and at the same time increases the dispersion of pigments is bodied linseed oil. McMillen<sup>60</sup> points out that paint at a shearing stress below its yield value must be considered a gel; above the yield value, it must likewise be considered a sol. Upon the removal of the higher shearing stress, the sol reverts to the gel condition. In this sense, therefore, paints exhibit thixotropic phenomena.

Oil paints, which are essentially suspensions of pigments in a non-volatile liquid medium, must not remain fluid too long while being brushed else they will flow due to the action of gravity and all leveling power would be lost. Reasonably quick solidification is necessary apart from the other physical and chemical effects of drying. This initial solidification is due to thixotropy. If the solidification is too rapid, brush marks will remain due to the fact that surface tension forces have been arrested.

An oil color varnish represents a very complex colloidal system in which a large number of colloids are simultaneously present. It ordinarily consists of oils, resins, thinners, driers and pigments, each of which can be considered colloidal. The changes which take place on drying either by oxidation or polymerization likewise give rise to colloidal material. Moreover, in such a system the colloids may be of the irreversible and of the reversible types. The latter may in a sense function as a protective colloid. In the making of a varnish, the resins must be first heated in order to break down the complex molecule into more simple components in order that they can be dispersed. If the resins are insufficiently heated before they are dispersed, some of the particles may be thrown out of solution. Oils are then added together with driers and thinners. On aging, certain components are precipitated leaving the varnish which is thus rendered less viscous but of easier working properties. Upon loss of the solvent, a

<sup>55</sup> A. de Waele, *J. Rheology*, 1920, 1, 139; *Chem. Abs.*, 1930, 24, 2023.

<sup>57</sup> E. C. Bingham and H. Green, *Proc. Am. Soc. Testing Materials*, 1919, 19 (2), 640; *Chem. Abs.*, 1920, 14, 1047.

<sup>58</sup> R. V. Williamson, G. D. Patterson and J. K. Hunt, *Ind. Eng. Chem.*, 1929, 21, 1111.

<sup>59</sup> E. L. McMillen, *Ind. Eng. Chem.*, 1931, 23, 677.

<sup>60</sup> E. L. McMillen, *Ind. Eng. Chem.*, 1931, 23, 676.

resin-like layer is obtained, a layer which behaves like a gel in one sense and not unlike glass in another.<sup>61</sup>

Wolff<sup>62</sup> has discussed the colloidal chemistry problems of varnish making. When lead resinate is dissolved in linseed oil at 150°C. to increase the rate of drying, a precipitate may form slowly or not at all owing to the mucilaginous material in the oil. The presence of a protective colloid was deduced by Schlick<sup>63</sup> who found that Prussian blue settled rapidly when ground with benzene. When the color was ground in with a small amount of linseed oil and then diluted with benzene, a clear blue solution was obtained which passed unchanged through filter paper. On filtering through a collodion ultrafilter, a colorless solution resulted.

Microscopic observations on drying color varnish films invariably show the development of a distinctly cellular structure, usually within 2-10 minutes after application of the varnish. Bartell and Van Loo<sup>64</sup> consider such development to be a vortex-ring action produced and maintained by volatilization of the solvent which causes a localized decline in temperature and change in density of the film. The action ceases when most of the volatile constituents have escaped and the rigidity of the remaining film has increased. The ideal varnish, they believe, should possess enough fluidity after loss of the volatile thinner to permit sufficient flow to eliminate all evidence of the cellular structure and to effect even distribution of the pigment. Various defects observed in color varnish films are explained by them<sup>65</sup> on the basis of this vortex-ring action. Pitting arises from high interfacial tensions between the varnish and the applied surface, from the repulsion of the varnish from nuclei (precipitated from the oil body) with the same electrical charge, and from the vortex action which may leave the centers of the cells as open pores in the films. Seeding is due to the accumulation of the pigment on immiscible solids suspended in the oil, to insufficient wetting of the pigment by the oil body, and to vortex action which piles up the denser or larger particles at the centers or corners of the cells. Silting results from the regular alignment of cells in the varnish film coupled with the same vortex action which causes seeding. Surface dulling is caused by the interference of light from the uneven-celled surface of the film, the accumulation of the pigment or other immiscible phase at the air interface, and the addition of water to the mixed varnishes.

#### COLLOIDAL PHENOMENA

It has been noted that in an amorphous substance a gradual transformation occurs between the solid and the liquid states. At a certain temperature, therefore, the forces between certain molecules will have been overcome whereas other molecules will still cohere to the solid mass. The result is a mixture of "liquid" and "solid" particles and may be considered an "isocolloid," in other words there are freely moving molecules present near fixed ones. Moreover, if under the influence of heat molecules of a liquid can combine chemically with one another (either by polymerization or condensation) with the formation of larger molecules, complexes will eventually be formed where thermal agitation ceases. When-

<sup>61</sup> Cf. H. A. Gardner, "Colloidal Phenomena in Paint and Varnish Products" in J. Alexander, "Colloid Chemistry," 1932, IV, 491.

<sup>62</sup> H. Wolff, *Z. angew. Chem.*, 1922, 35, 555; *Chem. Abs.*, 1923, 17, 344.

<sup>63</sup> W. Schlick, *Farben-Ztg.*, 1922, 27, 1792, 1873; *Chem. Abs.*, 1922, 16, 2232. See R. Schlick, *German P.* 442,650, 1924; *Brit. Chem. Abs. B.*, 1927, 447.

<sup>64</sup> F. E. Bartell and M. Van Loo, *Ind. Eng. Chem.*, 1925, 17, 925.

<sup>65</sup> F. E. Bartell and M. Van Loo, *Ind. Eng. Chem.*, 1925, 17, 1051.

ever there are freely moving molecules (i.e., liquid) co-existent with fixed molecules (i.e., solid), an isocolloid is again formed.<sup>66</sup>

Resins, as a rule, are not composed of single entities but consist of macromolecules of varying size. Resins can thus be considered as gels of highly polymerized organic substances where the disperse phase consists of a more highly polymerized form of the material composing the continuous phase.<sup>67</sup>

Another classification which has been made of these high-molecular-weight organic compounds is to call them "xerogels." These are gels which have been formed by drying. They are poor in liquid but are nevertheless coherent.<sup>68</sup> The term has also been applied to such natural colloids as cotton, wool, silk, hair, horn and to such artifacts as gelatin, leather, charcoal and cellulose derivatives (esters, ethers and the like) and to completely synthetic products such as phenol-formaldehyde resins and silica gel.<sup>69</sup>

The question as to just how many phases exist in gels is one which has been debated for a long time. Procter<sup>70</sup> postulated a one-phase theory on the basis of his results on the system, water-acid-gelatin in which equilibrium resulted from the combination of the gelatin and acid to form easily dissociable salts. The one-phase theory has also found support in Sutherland's<sup>71</sup> concept of chain molecules and in McBain's<sup>72</sup> view that identical colloidal particles are present in the sol and gel state.

Hardy<sup>73</sup> on the basis of microscopical study of gelatin concluded that the solid phase of gelatin consisted of a solid solution of gelatin in water. Gelation was essentially the separation of the sol into a solid open framework with an interstitial fluid phase. Ostwald<sup>74</sup> injected the concept of the two-phase liquid-liquid theory and this has been accepted by Bancroft.<sup>75</sup>

The third possibility remains that gels have a solid crystalline phase. This theory was originally proposed as early as 1835 by Frankenheim<sup>76</sup> and revived in 1858 by von Nägeli.<sup>77</sup> Gels were considered to be composed of molecular complexes, or micellae, with crystalline properties; the water being held by attraction in the interstices within and between the micellae. Butschli<sup>78</sup> introduced the idea that there were definite pores in the jelly and van Bemmelen<sup>79</sup> extended his concept to one where this cell-like structure was one of definite form hanging together forming a network. The more concentrated solution acted as a network of cell walls enclosing a more dilute solution of the same substance.

This concept of the crystalline structure existing in gels was studied by Scherrer<sup>80</sup> by means of x-rays. In certain of the rigid gels (silicic and stannic acids) there were well-marked interference patterns along with evidence of the amorphous state. The gelatin gel, however, yielded no evidence of crystallinity. These gels possess other characteristic dissimilarities. Silicic acid gel, on drying,

<sup>66</sup> R. Houwink, "Physikalische Eigenschaft und Feinbau von Natur- und Kunstharzen," Leipzig, Akad. Verlagsges., 1934; British Plastics Year Book, 1935, Plastics Press, Ltd., London

<sup>67</sup> There are, however, certain resins which consist of particles which are essentially of the same size. If all of the molecules were of the same size, then one would be dealing with liquids. Inasmuch as it is necessary to assume that in these liquids the particles are of colloidal dimensions, such liquid resins must be considered sols. Cf. R. Houwink, *loc. cit.*

<sup>68</sup> See H. Freundlich, "Colloid and Capillary Chemistry," trans. H. S. Hatfield, E. P. Dutton, New York, 1922, 600.

<sup>69</sup> Cf. S. E. Sheppard, *Trans. Faraday Soc.*, 1933, 29 (140), 77.

<sup>70</sup> H. R. Procter, *J.C.S.*, 1914, 105, 313.

<sup>71</sup> W. Sutherland, *Proc. Roy. Soc.*, 1907, 79, 130; *Chem. Abs.*, 1907, 1, 1861

<sup>72</sup> J. W. McBain, "3rd Report on Colloid Chemistry," Brit. Assoc. Adv. Sc., 1920, 2

<sup>73</sup> W. B. Hardy, *Proc. Roy. Soc.*, 1900, 66, 95, *J.C.S.*, 1900, 78 (2), 396.

<sup>74</sup> W. Ostwald, *Arch. ges. Physiol. (Pflüger's)*, 1905, 109, 277; 1906, 111, 581.

<sup>75</sup> W. D. Bancroft, "Applied Colloidal Chemistry," McGraw-Hill Co., New York, 1921, 239, 242.

<sup>76</sup> M. L. Frankenheim, "Die Lehre von der Kohäsion," Breslau, 1835. See *Ann.*, 1847, 72, 222.

<sup>77</sup> K. von Nägeli, "Pflanzenphysiologischen Untersuchungen," Zurich, 1858.

<sup>78</sup> Butschli, "Untersuchungen über Strukturen," Leipzig, 1898.

<sup>79</sup> J. M. van Bemmelen, *Z. anorg. Chem.*, 1898, 18, 14.

<sup>80</sup> P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1918, 96; *Chem. Abs.*, 1919, 13, 2624.

develops pores which contain air and these pores can be filled by imbibition.<sup>22</sup> Elastic gels (gelatin) do not develop such pores and the dried gels will not imbibe foreign liquids. The work of Katz and Gerngross,<sup>23</sup> however, suggests that there is a molecular orientation. In the x-ray diffraction spectrum obtained from dry gelatin films, a diffuse ring and a wide sharp ring occurring in the unstretched material changed on elongation. The sharp ring dissolved into two crescent shaped parts.

Von Weimarn<sup>24</sup> considers as a gel any liquid which assumes throughout its mass a half solid, elastic consistency, keeping at the same time in a more or less degree its former transparency. Jellies may be classified as follows: (1) according to the method of formation. This class includes network jellies (gelatin) which gelatinize uniformly throughout the mass and also membranous jellies which gelatinize only on definite interfaces between two liquids in the act of mixing. (2) They may be classed according to the degree of dispersity of the primary particles. In network jellies this includes macro-, micro-, ultramicro- and sub-ultramicrocrystalline jellies; in membranous jellies, ultramicro- and subultramicrocrystalline jellies. (3) Jellies may be considered with respect to their consistency as being resin-like pastes, soft-elastic or solid jellies (glasses) or (4) according to the concentration of the disperse part; or (5) according to whether they are temperature-reversible or temperature-irreversible. In the formation of membranous gels, it is necessary to have a high specific supersaturation and low solubility of the precipitating substance. The less the solubility, the longer the gel remains. Membranous gels, on shaking thoroughly, sometimes pass over into the network gel. In the formation of network gels, the solubility must be low, the specific supersaturation high and in addition there must be abundant solvation.

Thomas and Sibi<sup>25</sup> have found that when aqueous solutions of such compounds as sorbitol acetate, benzoyl cystine, benzoyl tyrosine, quinine sulphate, opto-quinine sulphate and the like, are cooled they form transparent gels which initially appear homogeneous under the microscope. On standing, or on the addition of organic solvents (alcohol or acetone), the gels are transformed into masses of crystals in the form of flexible, intertwining hairs. When stirred or shaken, the structure is destroyed. The separation of the dispersion medium offers an explanation for the general phenomenon of syneresis. The crystals separating from the dispersion medium may be filtered, dried, re-dissolved and cooled to again form a gel. These experiments favor the view that gels contain a solid phase.

All of the gels so far considered have been those which are dispersed in water. Whitby<sup>26</sup> has called attention to the fact that hydrophilic colloids are always treated with respect to water. Organophilic colloids bring in a new problem inasmuch as various organic liquids may be used. There should, however, be a relation between the swelling of substances and the structure of the liquids in which the immersion takes place. In the case of the swelling of rubber in solvents, it was found that compounds with an active group (nitrile, aldehyde or ketone) were more effective as the length of the hydrocarbon chain increased.

Mardles,<sup>27</sup> in a study of the solvents for cellulose esters, determined that hydrocarbons, ethers and the like exert little or no solvent action whereas such

<sup>22</sup> E. Hatschek, "The Viscosity of Liquids," G. Bell and Sons, Ltd., London, 1928.

<sup>23</sup> J. R. Katz and O. Gerngross, *Naturwissenschaft*, 1925, 13, 900; *Chem. Abs.*, 1926, 20, 528.

<sup>24</sup> P. P. von Weimarn, *Rep. Imp. Ind. Res. Inst. Osaka*, 1928, 9, 13; *Chem. Abs.*, 1928, 22, 4029.

See W. Ostwald, *Kolloid-Z.*, 1928, 46, 248; *Chem. Abs.*, 1929, 23, 1334, for another classification of gels.

<sup>25</sup> P. Thomas and M. Sibi, *Rev. gen. colloides*, 1930, 8, 68, 105; *Chem. Abs.*, 1930, 24, 5570.

<sup>26</sup> G. S. Whitby, "Colloid Symposium Monograph," Chem. Cat. Co., N. Y., 1926, 203.

<sup>27</sup> E. W. J. Mardles, *J.S.C.I.*, 1928, 42, 184T.

compounds as acetic acid, methyl formate or acetate, benzaldehyde, acetone, epichlorhydrin and ethyl tartrate are excellent solvents. Whitby<sup>87</sup> further points out that the solvents for cellulose esters are in general non-solvents for rubber.

In additional studies, it was found that polyvinyl acetate swells and disperses in organic liquids of high dielectric constant whereas polyacrylic acid is soluble in water and formamide but insoluble in acetone and alcohol. By treating the polymerized methyl acrylate with magnesium methyl iodide in anisole at 100°C., an impure tertiary alcohol is obtained.<sup>88</sup> This alcohol is soluble in alcohols and in benzene. The corresponding hydrocarbon is soluble in benzene and precipitated by ethanol.<sup>89</sup>

In further work with cellulose acetate, Mardles<sup>90</sup> traced the gelation in benzyl alcohol through three distinct stages: 1) the coalescence of fine particles into larger ones; 2) the aggregation of the large particles into clusters; and 3) the linkage of the clusters to a rigid gel structure. The reaction was measured by the equation

$$\eta - \eta_0 = \alpha e^{\kappa t}$$

$\eta$  is the apparent viscosity of the gelating sol

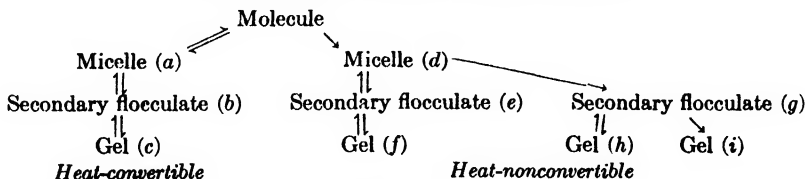
$\eta_0$  is the original viscosity of the sol,  $\alpha$ , depending on  $\eta_0$  and

$\kappa$  is the rate of gelation

The temperature at which  $\kappa$  becomes nil was taken as the maximum gelation temperature. Beyond this point the sol was relatively stable with time; below this point, part or whole of the dispersed particles aggregated to form a gel structure.

Wornum<sup>91</sup> has discussed the phenomenon of gelation on the basis of primary and secondary valence of the resin particle. The large molecules do not exist in the free state except in dilute solution. In more concentrated solutions, they exist as micelles. The molecules cannot be bound together except by the van der Waal forces and any micelle formed will be of an evanescent character. When secondary flocculates do form, the action is reversible (see Table 3—*a*, *b*, *c*). When the micelle (*d*) is built up by primary valence forces, it is not possible to disperse the mass without the rupture of bonds. Under conditions where no chemical interaction takes place (*e*, *f*), the forces are cohesive and the mass may be redispersed by using a proper solvent. When primary valence is involved, structures of varying degrees of complexity are built up (*g*, *h*, *i*) and can be redispersed only when cohesive forces are used to build up the particle (*h*).

TABLE 3.—Reversible and Irreversible Gelation.\*



⇌ indicates reversibility; involves secondary valence.

→ indicates irreversibility; involves primary valence.

\* W. E. Wornum, *loc. cit.*

<sup>87</sup> G. S. Whitby, J. G. McNallay and W. Gallay, "Colloid Symposium Monograph," 1928, VI, 225.

<sup>88</sup> See H. Staudinger and E. Urech, *Helv. Chim. Acta*, 1929, 12, 1107; *Brit. Chem. Abs. A*, 1930, 64.

<sup>89</sup> For a discussion of the choice of solvents for mixtures of pyroxylin and resins see R. Calvert, *Ind. Eng. Chem.*, 1929, 21, 213.

<sup>90</sup> E. W. J. Mardles, *Trans. Faraday Soc.*, 1923, 18, 327.

<sup>91</sup> W. E. Wornum, *J. Oil, Colour Chem. Assoc.*, 1933, 16, 231.

Wornum has extended this concept to the formation of films. Where the oxidation of tung oil is rapid, the flocculates are small in size and the oil sets to a clear film. The webbing of tung oil is considered to be due to the random coagulation of the large flocculates. When partial orientation has a chance to take place, there is local coagulation resulting in the formation of small irreversible gel particles. This leads to a crystalline or "frosty" appearance. In the heat-bodying of tung oil at temperatures below 270°C., the acid in the  $\beta$ -position of glyceride has not sufficient energy to allow primary cross-valency to take place. It is only when the temperature reaches approximately 270° that cross-linkages occur with any ease and under the conditions flocculate growth occurs. Higher temperatures (310°) cause a very much greater increase in the number of cross-linkages which can take place with the result that a large number of small flocculates form. In under-cooked tung oil, the  $\beta$ -position has not been used. This favors the formation of large flocculates and hence "webbing." "Blooming" of the film is ascribed by Wornum to be due to the swelling of the large particles by water. Linseed oil has little tendency to produce large flocculates and consequently there is no tendency toward webbing. Varnishes can thus be divided into two types depending on whether the disperse phase consists of a large number of small flocculates or a small number of large flocculates.

Other factors also enter. The concept of a monomolecular film on a surface has become familiar from the work of Langmuir,<sup>82</sup> Adam<sup>83</sup> and others, and it is a well-established observation that in such a film the molecules may be oriented (e.g., in the case of substances with chain-like molecules, they may all be on end or tilted). Tammann<sup>84</sup> has concluded that the power of orientation in a film is restricted to those molecules which are able, under the conditions of the experiment, to undergo crystallization.<sup>85</sup>

High-molecular-weight organic substances behave differently from the fatty acids when spread on surfaces. Measurements were made on the thickness of the thinnest coherent films obtained by the evaporation of dilute solutions of macropolymers upon a mercury surface. The results are given in Table 4.

TABLE 4.—Films of Polymers <sup>a</sup>

Substance	Solution	Comparative Viscosity	Film Thickness
Rubber..	Ether		1.5 Å
Gelatin.	Water		7.0
Cellulose diacetate	Acetone		4.1
			3.8
			4.2
Cellulose triacetate	Chloroform	1960.0	9.85
Cellulose nitrate	Acetone	3025.0	2.50
		776.0	3.60
		13.5	4.23
		2.1	4.50
		0.2	5.00

<sup>a</sup> S. E. Sheppard, A. H. Neitz and R. L. Krenau, *Ind. Eng. Chem.*, 1929, 21, 126

Comparison of these values with the thickness of the monomolecular films obtained for the fatty acids (e.g., stearic acid, 22 Å.u) reveals that the large

<sup>82</sup> I. Langmuir, *J.A.C.S.*, 1917, 39, 1348; I. Langmuir and D. B. Langmuir, *J. Phys. Chem.*, 1927, 31, 1719; *Chem. Abs.*, 1928, 22, 522.

<sup>83</sup> N. K. Adam, *Chem. Reviews*, 1926, 3, 163.

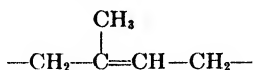
<sup>84</sup> G. Tammann and H. E. Gronow, *Z. anorg. Chem.*, 1930, 194, 268; *Brit. Chem. Abs.*, A, 1931, 163. See A. V. Blom, *Kolloid-Z.*, 1931, 54, 210; *Brit. Chem. Abs.*, A, 1931, 422.

<sup>85</sup> R. E. Wilson and E. D. Ries, "Colloid Symposium Monograph," Dept. Chem., U. of Wisconsin, 1923, I, 145, found that liquids in thin films take on the properties of plastic solids.



molecules are exceedingly thin.<sup>66</sup> It has been concluded that the values found represent the transverse dimensions of the long chain-like or the sheet forms of the molecules which are orientated parallel to the surface rather than end-on as in the fatty acids. Inasmuch as in the high-molecular-weight compounds the chains are repetitions of certain units, there will be a potential alternating polarity along the chain, each periodic element containing both a polar and a non-polar grouping. This condition becomes accentuated as parallel orientation of the chain occurs. Where this takes place, the alternating polarity levels up the chains so that the sub-chains can form a space lattice.

The dimensions of the rubber film approximate the methyl group in rubber



which is about 1.5 Å. In the case of cellulose nitrate there appears to be a relation between the viscosity and the thinness of the limit film. Where the chains are short, the tendency will be toward vertical piling and overlapping. This also occurs in the case of proteins.<sup>67</sup>

<sup>66</sup> R. L. Keenan, *J Phys Chem*, 1929, 33, 371 S E. Sheppard and R C Houck, *J Rheol*, 1929, 1, 20.

<sup>67</sup> E Gorter and F Grendel, *Proc K Akad Wetensch Amsterdam*, 1929, 32, 770; *Brit. Chem. Abs. A*, 1929, 1141.

## Chapter 4

### Nature of Resin Formation. Polymerization and Condensation. Fiber Structures. X-Ray Methods.

In order to prepare resinous compounds it is necessary to start with substances of rather low molecular weight. The transformation of various low-molecular-weight compounds into complex derivatives is usually termed "polymerization,"<sup>1</sup> but in this polymerization, two very distinct types of reactions can be distinguished: one which, for lack of a better term, is called polymerization and the other condensation. In a polymerization reaction the reactants are marked by a large degree of unsaturation and the resulting more saturated polymer is a multiple of the initial reactant, in other words the percentage composition remains unaltered. In condensation reactions, on the other hand, the final product is no longer a multiple of the monomer and in order to obtain the formula of the final condensate it is necessary to subtract the sum of the simple compounds which have been liberated during the condensation. Polymerization has been defined in various ways. Staudinger<sup>2</sup> considered polymerization as the union of like molecules to form a product of the same composition. Carothers<sup>3</sup> defined polymerization as the chemical combination of a number of similar units to form a single molecule; this definition embraced not only the condensation reaction but the true polymerization phenomena.

Other types of polymerization occur however, for example the "heteropolymerization" with which the name Wagner-Jauregg is associated and also copolymerization. Moreover, little distinction is made in the use of the term between the polymerization which involves comparatively few molecules and the polymerization wherein a great number of molecules enter into the formation of a single complex. Polymerization is used to designate the transformation of acetaldehyde to paraldehyde and the formation of polystyrene from styrene.

The term polymerization in this chapter will be used in the sense of macropolymerization and a distinction will be made between condensation and polymerization. The following types will be considered (1) addition or homopolymerization together with co-polymerization and heteropolymerization and (2) multicondensation. Among the polymerization polymers can be included such compounds as olefins, polyolefins and unsaturated compounds whereas multicondensation takes into account such reactions as polyesters, phenol-aldehydes and the like.

#### CLASSIFICATION OF POLYMERIZATION AND CONDENSATION

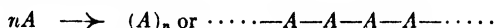
*Additive or homopolymerization* is a species of polymerization in which the

<sup>1</sup> R. H. Kienle and A. G. Hovey (*J.A.C.S.*, 1929, 51, 509) believe that the study of resin formation will develop new ideas concerning stereochemistry and bring about a better correlation between organic chemistry, colloidal phenomena and statistical mechanics.

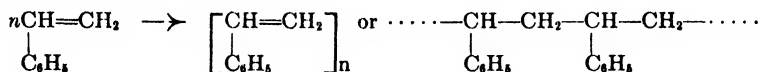
<sup>2</sup> H. Staudinger, *Ber.*, 1920, 53, 1073.

<sup>3</sup> W. H. Carothers, *J.A.C.S.*, 1929, 51, 2546.

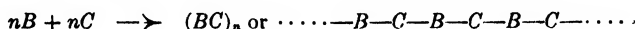
polymer is built up by the additive combination of the monomer. The process may be shown schematically as:



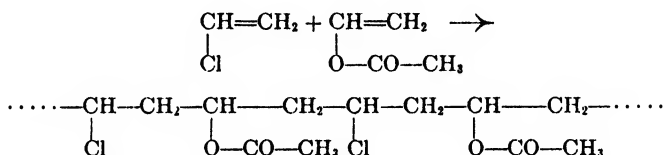
where "n" represents the number of monomeric groups of A, the monomeric unit. Since all of the groupings are alike, this is termed homopolymerization. For example, styrene ( $C_6H_5CH=CH_2$ ) on heating forms a resin of composition  $(C_8H_8)_n$  which may be represented:



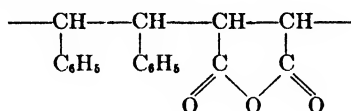
*Co-polymerization* is the term applied when two or more substances polymerize at the same time to yield a product which is not necessarily a mixture of polymers; its properties differ from that of either polymer alone. The reaction may be considered to take place



or



*Heteropolymerization* is a special case of additive co-polymerization which involves the combination of a polymerizable, i.e., unsaturated substance and another unsaturated substance which by itself does not readily polymerize. Though maleic anhydride does not ordinarily polymerize, it will combine with stilbene in boiling xylene to yield a white amorphous heteropolymer in which the combining ratio is 1:1.<sup>4</sup> The structure has been represented as:



Condensation reactions take a variety of forms in the same manner as the addition polymerization types. A discussion of this type of reaction will be considered subsequently together with those reactions where additive polymerization and condensation occur together.

#### CHEMICAL STRUCTURE AND POLYMERIZATION

Both the physical and chemical concepts of the molecule have been used to account for ready ease of additive polymerization. One school considers that the resinous state is governed entirely by physical conditions; another that it is wholly due to definite chemical groups. Still another that it is a matter of chemical structure of the entire molecule.

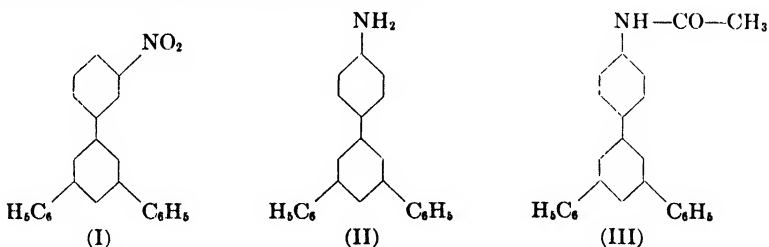
Scheiber<sup>5</sup> emphasizes the purely physical aspects of resinification and considers

<sup>4</sup> T. Wagner-Jauregg, *Ber.*, 1930, 63, 3213.

<sup>5</sup> J. Scheiber, *Farbe u. Lack*, 1929, 86, 102; *Chem. Abs.*, 1929, 23, 2583; *Chem. Umschau*, 1928, 35, 181; *Chem. Abs.*, 1929, 23, 1867. See also *Farbe u. Lack*, 1927, 67; *Brit. Chem. Abs. A*, 1928, 1100. *Chem. Ztg.*, 1929, 53, 643; *Chem. Abs.*, 1929, 23, 5599.

the resinous state to be due to the formation of solid solutions (undercooled fusions) or to the formation of colloidal aggregates through condensation or polymerization. In these solid solutions and colloidal complexes, the orientation velocity lags behind the velocity with which irregular molecular complexes form.<sup>6</sup> Fonrobert<sup>7</sup> likewise characterizes the resinous state as a mixture of similar high-molecular-weight compounds. That high-molecular-weight substances have a profound effect on the velocity of crystallization from solution can not be questioned in the light of the experiments of Marc.<sup>8</sup>

Other factors, nevertheless, are in evidence. If the molecule contains groups which tend to destroy its symmetry, this fact will in itself favor resin formation. Vorländer<sup>9</sup> has noticed that para-substitution in the benzene nucleus tends to give rise to the liquid crystal or mesomorphic state of matter; the formation of liquid crystals he considers a manifestation of molecular regularity. The predominantly one-dimensional state is one of the most important factors for the formation and cohesion of anisotropic crystals inasmuch as the linear molecule has the greatest stability with the closest parallel packing.<sup>10</sup> The formation of supercooled liquids, on the other hand, is favored by those influences which prevent the formation of liquid crystals.<sup>11</sup> These influences include branched chains, an uneven number of side chain groupings and meta- and ortho-substitution; in other words, factors which bring about a dissymmetry in the molecule and tend to make it more difficult for a substance to solidify into the crystalline form. Under all conditions s-triphenylbenzene solidifies from the amorphous molten condition to a solid crystalline mass without marked undercooling. If the hydrocarbon is brominated, nitrated or aminated, the substituted products, in consequence of the dissymmetry of the molecule, form on rapid cooling transparent colorless amorphous lacs which remain in this condition at 15-20°C. On warming, the lacs become crystalline solids.<sup>12</sup> Triphenylmethane derivatives ( $C_6H_5$ )<sub>3</sub>C-X are dissymmetrical and such substances remain permanently in a supercooled amorphous state.<sup>13</sup> This view on the cause of resinification is also supported by data on such compounds as 1-nitrophenyl-3,5-diphenylbenzene (I), 1-p-aminophenyl-3,5-diphenylbenzene (II) or 1-acetyl-p-aminophenyl-3,5-diphenylbenzene (III).



These substances yield amorphous resins on supercooling.<sup>14</sup>

<sup>6</sup> See Chapter 3.

<sup>7</sup> E. Fonrobert, *Chem. Ztg.*, 1934, 29, 247, 273; *Chem. Abs.*, 1934, 28, 3252.

<sup>8</sup> R. Marc, *Z. Elektrochem.*, 1909, 15, 679; *Chem. Abs.*, 1910, 4, 9. *Z. physik. Chem.*, 67, 470, 640; *Chem. Abs.*, 1910, 4, 404. R. Marc and W. Wenk, *ibid.*, 68, 104; *Chem. Abs.*, 1910, 4, 404. R. Marc, *ibid.*, 73, 685; *Chem. Abs.*, 1910, 4, 2899. *Ibid.*, 75, 710; *Chem. Abs.*, 1911, 5, 1225. *Ibid.*, 79, 71; *Chem. Abs.*, 1912, 6, 3042.

<sup>9</sup> D. Vorländer, *Z. angew. Chem.*, 1922, 35, 249; *Chem. Abs.*, 1922, 16, 2800.

<sup>10</sup> D. Vorländer, *Trans. Faraday Soc.*, 1933, 29, 899. See J. R. Katz, *Naturwiss.*, 1928, 16, 758; *Brit. Chem. Abs. A*, 1928, 312 for x-ray diffraction patterns of liquids and liquid-crystals.

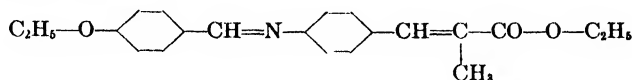
<sup>11</sup> D. Vorländer, *Z. physik. Chem.*, 1923, 105, 211; *Chem. Abs.*, 1924, 18, 1072.

<sup>12</sup> D. Vorländer, E. Fischer and H. Wille, *Ber.*, 1929, 62, 2836; *Brit. Chem. Abs. A*, 1930, 79.

<sup>13</sup> D. Vorländer, *Ber.*, 1925, 58, 1893; *Chem. Abs.*, 1926, 20, 584.

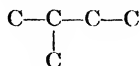
<sup>14</sup> D. Vorländer, *Z. angew. Chem.*, 1930, 43, 13; *Chem. Abs.*, 1930, 24, 4944.

By the ramification and bifurcation of the side chains, the molecule may become large enough in size to remain stationary. Vorländer<sup>15</sup> has shown that by increasing the size of the linear molecule, which decreases the tendency toward crystallization, it is possible to form liquid-crystal resins and lacquers. A substance of this type is as follows:



The formation of varnishes by polymerization and oxidation appears to be due to a decrease in the symmetry of the molecule which permits permanent supercooling or hardening of the amorphous mass. Something of this nature exists in drying oils. The ideal molecular structure to impart film-forming properties according to Scheifele<sup>16</sup> should consist of a central nucleus bearing three radiating thread-like groups. This structure is approached by linolenodihmolein and by cellulose esters.

Boekenooen<sup>17</sup> has drawn attention to the unsymmetrical arrangement of carbons



which can be found in many natural resins, gums and rubber. It appears as if nature had a special preference for this grouping in building up highly polymerized compounds.<sup>18</sup>

The presence of certain unsaturated groups, however, seems to be necessary for the occurrence of a reaction in an addition polymerization. The particular methods of effecting the reaction and the complex which can be formed depend on other factors than unsaturation alone.

Herzog<sup>19</sup> coined a term, "resinophore," for groups responsible for resinous properties. This term was first used with the carbodiimide grouping and was later extended to conjugated linkages.<sup>20</sup> Eibner<sup>21</sup> proposed to restrict the use of the term resinophore for the structural group present in the actual resin and introduced the word "resinogen" for the potential group. The presence of a resinogen in a molecule does not mean that a molecule is a resin but that under suitable conditions it may form one. Wolff,<sup>22</sup> on the other hand, considers resinogens as groups which tend to form compounds of high molecular weight but believes resins to be the result of conditions rather than of certain chemical groups.<sup>23</sup>

<sup>15</sup> D. Vorländer, *Trans. Faraday Soc.*, 1933, 29, 907. See also D. Vorländer, *Ber.*, 1908, 41, 2046; 1934, 67, 1556; *Chem. Abs.*, 1908, 2, 2798, 1935, 29, 1400.

<sup>16</sup> B. F. H. Scheifele, *Fette Umschau*, 1933, 40, 141; *Brit. Chem. Abs. A.*, 1933, 1010.

<sup>17</sup> H. A. Boekenooen, *Verf.kroniek*, 1932, 25 (6), 13, 15, 17; *Chem. Abs.*, 1932, 26, 4600.

<sup>18</sup> The presence of this group in natural products may arise from the fact that nature leans toward isoprene as a structural unit.

<sup>19</sup> W. Herzog, *Oester. Chem. Z.*, 1921, 24, 76; *J. S. C. I.*, 1921, 40, 478A.

<sup>20</sup> W. Herzog and J. Kriedl, *Z. angew. Chem.*, 1922, 35, 465; *J. S. C. I.*, 1922, 41, 771A. *Ibid.*, 1922, 35, 641; *J. S. C. I.*, 1922, 41, 988A.

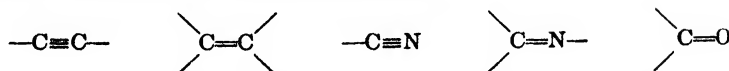
<sup>21</sup> A. Eibner, *Z. angew. Chem.*, 1923, 36, 33; *Chem. Abs.*, 1923, 17, 3796. *Ibid.*, 1924, 37, 288; *Chem. Abs.*, 1924, 18, 2611.

<sup>22</sup> H. Wolff, *Z. angew. Chem.*, 1927, 40, 1010; *Chem. Abs.*, 1928, 22, 3055.

<sup>23</sup> R. Oda (*Nia Kémio*, 1932, 5, 47; *Chem. Abs.*, 1932, 26, 2711) has developed a theory that in unsaturated compounds polymerization can occur only where there is a permanent dipole moment. Unsaturated compounds first arrange themselves to have a minimum electrical moment and then the union of chemical bonds takes place.

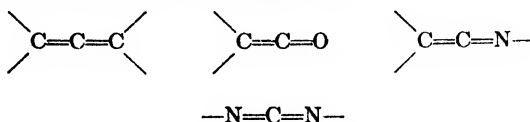
Autocatalysis has been considered by I. L. Kondakov (*Chem. Listy*, 1930, 24, 271, 293; *Chem. Abs.*, 1930, 24, 4933) to be a special variety of catalysis produced by the action of molecules of the same substance without the interaction of foreign substances. Autocatalyzable substances are characterized by unsaturated bonds or possess an unstable ring.

Broadly speaking any unsaturated grouping

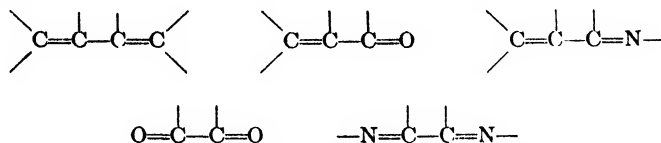


acts as a polymerizing factor. The capacity for resinification is determined, however, not only by the grouping itself but also on external factors, among which can be mentioned heat, light, pressure and catalysts.

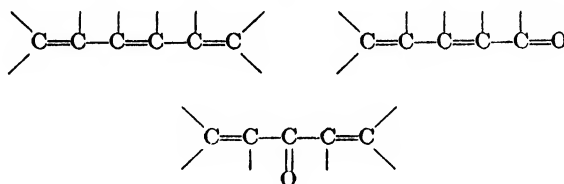
If all of the unsaturation is on a single atom,



the tendency for polymerization is greater. Conjugation of the groupings is even more effective



Additional conjugation further increases the tendency toward polymerization



Compounds like styrene which contain a negative group attached to the vinyl radical tend to form polymers in which the degree of polymerization is very high. Other negative groups include:

Group	Compound	Reference
Carboxyl . . . . .	$\text{CH}_2=\text{CH}-\text{COOH}$	Acrylic acid (24)
Aldehyde . . . . .	$\text{CH}_2=\text{CH}-\text{CHO}$	Acrolein (25)
Acetyl . . . . .	$\text{CH}_2=\text{CH}-\text{CO}-\text{CH}_3$	Methyleneacetone (26)
Acetoxy . . . . .	$\text{CH}_2=\text{CH}-\text{O}-\text{CO}-\text{CH}_3$	Vinyl acetate (27)
Ethoxy . . . . .	$\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_3$	Vinyl ethyl ether (28)
Chloride . . . . .	$\text{CH}_2=\text{CH}-\text{Cl}$	Vinyl chloride (29)

Certain substituents have a definite effect in the ethylene group and greatly lessen the tendency to polymerize.<sup>20</sup> A methyl group on the ethylene has a pro-

<sup>20</sup> H. Staudinger and E. Urech, *Helv. Chim. Acta*, 1929, 12, 1107; *Chem. Abs.*, 1'30, 24, 2720. See Chapter 53

<sup>21</sup> C. Moureu and C. Dufraise, British P. 141,058, 1920; *J.S.C.I.*, 1921, 40, 858A. See Chapter 23.

<sup>22</sup> German P. 309,224, 1917, to F. Bayer & Co.; *J.S.C.I.*, 1920, 39, 624A. See Chapter 25.

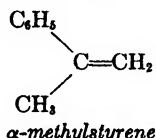
<sup>23</sup> H. Staudinger, K. Frey and W. Starck, *Ber.*, 1927, 60, 1782; *Chem. Abs.*, 1928, 22, 215. See Chapter 51.

<sup>24</sup> J. Wislicenus, *Ann.*, 1878, 192, 108; *J.C.S.*, 1878, 34, 776. See Chapter 50.

<sup>25</sup> E. Baumann, *Ann.*, 1872, 163, 308; *Chem. Zentr.*, 1873, 28. See Chapter 51.

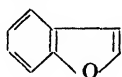
<sup>26</sup> R. Kuhn and A. Winterstein (*Helv. Chim. Acta*, 1928, 11, 87; *Chem. Abs.*, 1928, 22, 1767) have shown that the union of the end valencies of butadiene and isoprene with a phenyl group destroys completely the tendency to polymerize, and allows the study of these polyenes. They prepared a series of derivatives from stilbene ( $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ ) to diphenyl hexadecaoctaene ( $\text{C}_6\text{H}_5-\text{CH}=[\text{CH}-\text{CH}]_7-\text{CH}-\text{C}_6\text{H}_5$ ). For the influence of carboxyl and carbalkoxyl groups in butadiene and their influence on polymerization, see K. Vogt, *Mitt. schweizerischen Kohlenforsch. Kaiser-Wilhelm Ges.*, 1925, 2, 69; *Chem. Zentr.*, 1926, 1, 2340; *Chem. Abs.*, 1927, 21, 3890.

found effect:  $\alpha$ -methylstyrene<sup>21</sup> forms an octamer whereas  $\beta$  methylstyrene<sup>22</sup> yields



only the dimer. Substituents in the phenyl group have little or no effect.<sup>23</sup>

The ethylene group may exist in a ring and still retain its ability to polymerize. Thus, cumarone,<sup>24</sup> indene,<sup>25</sup> cyclopentadiene<sup>26</sup> and pyrrole<sup>27</sup> will form polymers but do not build giant molecules.



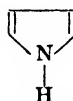
cumarone



indene



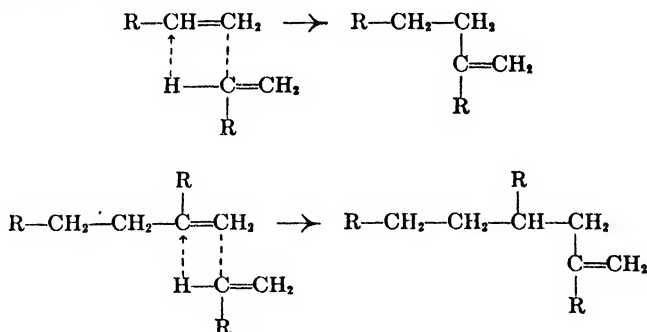
cyclopentadiene



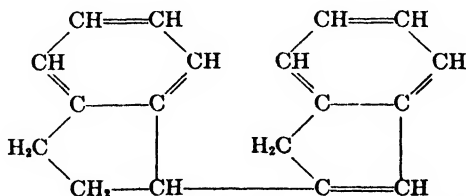
pyrrole

#### MECHANISM OF ADDITION POLYMERIZATION

The reaction mechanism of addition polymerization may most easily be shown by the migration of a hydrogen atom:



Partial credence to this hypothesis has been given by the isolation of diindene of the structure<sup>28</sup>



<sup>21</sup> H. Staudinger and F. Breusch, *Ber.*, 1929, 62, 442; *Chem. Abs.*, 1929, 23, 3213.

<sup>22</sup> G. Errera, *Gazz. chim. ital.*, 1896, 14, 509; *J.C.S.*, 1895, 43, 772.

<sup>23</sup> See Chapter 11 for a further discussion.

<sup>24</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 81. See Chapter 5.

<sup>25</sup> H. Staudinger, A. A. Ashdown, M. Brunner, H. A. Bruson and S. Wehrli, *Helv. Chim. Acta*, 1929, 12, 964; *Chem. Abs.*, 1929, 24, 612.

<sup>26</sup> H. Staudinger and H. A. Bruson, *Ann.*, 1926, 447, 97. Cf. Chapter 40 and K. Alder and G. Stein, *Ann.*, 1932, 496, 204.

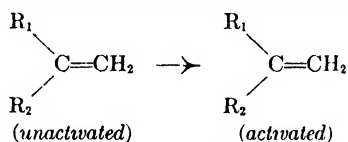
<sup>27</sup> B. V. Tronov and P. P. Popov, *J. Russ. Phys.-Chem. Soc.*, 1926, 58, 745; *Brit. Chem. Abs. A.* 1927, 775.

<sup>28</sup> H. Stobbe and E. Färber, *Ber.*, 1924, 57, 1838; *Chem. Abs.*, 1925, 19, 492.

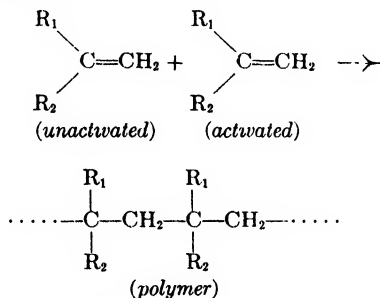
which one may consider to have been formed by the wandering of a hydrogen atom.<sup>39</sup> The continual action of the molecules of the unsaturated polymer would ultimately give rise to a long chain molecule or macropolymer.

Chalmers<sup>40</sup> has pointed out that the stepwise theory of polymerization is quite inadequate to explain macropolymerization. If the rate of consecutive reactions in a polymerization is not greater than dimerization, it naturally follows that the dimer and other low polymers should be formed in the largest proportion. Moreover it should be possible to isolate the intermediate di-, tri- and tetramers during a reaction macropolymerization. The absence of lower polymers at the beginning of and during the reaction has been noticed by Stobbe and Posnjak<sup>41</sup> in the conversion of styrene, by Stobbe and Lippold<sup>42</sup> in regard to ethyl itaconate and by Lebedev and Mereshkowski<sup>43</sup> in the polymerization of diolefinic hydrocarbons.

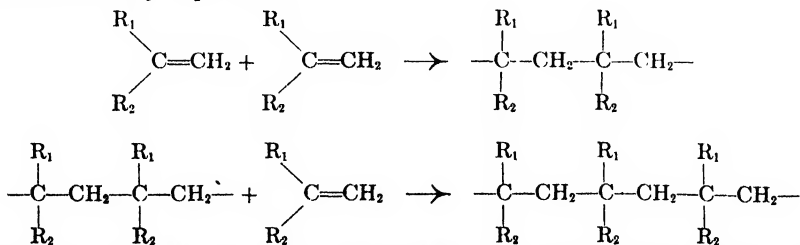
The mechanism postulated for polymerization reactions is as follows.<sup>44</sup>



The reaction rate of this instance is comparable with those of the ordinary reactions of organic compounds. The following reaction, leading to the polymeric form is practically instantaneous:



A somewhat similar proposal has been made by Staudinger<sup>45</sup> wherein each of the polymers has free terminal bonds (free radicals) and the reaction is imagined to proceed at a very rapid rate.



<sup>39</sup> G. S. Whitby and M. Katz, *Can. J. Research*, 1930, 4, 344; *Chem. Abs.*, 1931, 25, 3988; *J.A.C.S.*, 1929, 51, 2548.

<sup>40</sup> W. Chalmers, *J.A.C.S.*, 1934, 56, 912.

<sup>41</sup> H. Stobbe and G. Posnjak, *Ann.*, 1909, 371, 269, 295; *Chem. Abs.*, 1910, 4, 2120.

<sup>42</sup> H. Stobbe and A. Lippold, *J. prakt. Chem.*, 1914, 90, 336; *Chem. Abs.*, 1915, 9, 209.

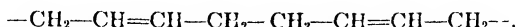
<sup>43</sup> S. V. Lebedev and B. K. Mereshkowski, *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 1357; *Chem. Abs.*, 1914, 6, 320.

<sup>44</sup> W. Chalmers, *Can. J. Res.*, 1932, 7, 113.

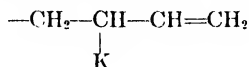
<sup>45</sup> H. Staudinger, *Ber.*, 1920, 53, 1081.



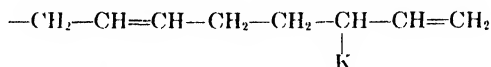
The linking of the monomeric units would be expected to proceed at a rate which would be almost instantaneous as compared with that of activation. With very great chains, the rate should be increasingly slow. The macropolymerization of butadiene and other diolefins would be through the formation of pseudo-molecules of the type



In certain instances in the polymerization of diolefins where the action is catalyzed by an alkali metallic compound (R-K), the reaction may be explained by the hypothesis that the primary compound



is in itself an alkali metallic compound and can react with a molecule of butadiene to yield



and the process continues.<sup>46</sup> In this instance the potassium alkyl acts as a trigger for polymerization.<sup>47</sup> The polymerization of vinyl acetate follows a unimolecular rate. Benzoyl peroxide acts as a trigger catalyst.<sup>48</sup>

Tammann and Pape<sup>49</sup> studied the effect of pressure on the polymerization of styrene, isoprene, vinyl acetate, dimethylbutylene and indene. In these polymerizations there is first a decrease in volume. The decrease in pressure at constant volume was taken as a measure of the reaction velocity and it was found that the reaction behaved unimolecularly. The pressure-temperature curves show first a linear rise, then a break where polymerization begins, a sharp fall during polymerization, whereupon there is another rise due to the expansion of the polymer. Increasing pressure causes a decrease in the temperature at which polymerization occurs.

Starkweather<sup>50</sup> also studied the polymerization of a number of compounds at high pressures (2000-9000 atmospheres) at a temperature of 20-74°C. Among the compounds subjected to pressure were 4-iodo-1,2-butadiene, 2-bromo-1,3-butadiene, 2-chloro-1,3-butadiene, methyl vinyl ketone, 2-phenyl-1,3-butadiene, 1,4-dichloro-2,3,5-hexatriene, divinylacetylene, 2-heptyl-1,3-butadiene, styrene, isoprene, methylethylvinylethynylcarbinol and the like. The rate of polymerization by substituent groups in the  $\beta$ -position of the dienes is in the order of alkyl, phenyl, chloro, bromo and iodo. In the  $\alpha$ -position, the halogens are less effective whereas the alkyl groups are inhibitory.<sup>51</sup> Samples of cracked gasoline under high pressure gave no indication of any resinous products although the distillation range indicated that about 10 per cent of the low-boiling material had been converted into higher-boiling compounds.<sup>52</sup> A series of experiments with tung oil revealed that polymerization occurred at 500-600 atmospheres and 50°C. to yield products similar to those formed at much higher temperature at atmospheric pressure. Tung oil under pressure for three hours became more viscous. Longer subjection to

<sup>46</sup> K. Ziegler and H. Kleiner, *Ann.*, 1929, 473, 57; *Chem. Abs.*, 1929, 23, 5181. K. Ziegler and K. Bähr, *Ber.*, 1928, 61, 253; *Brit. Chem. Abs. A*, 1928, 404.

<sup>47</sup> W. Chalmers, *loc cit*

<sup>48</sup> H. W. Starkweather and G. B. Taylor, *J.A.C.S.*, 1930, 52, 4708.

<sup>49</sup> G. Tammann and A. Pape, *Z. anorg. allgem. Chem.*, 1931, 200, 113; *Chem. Abs.*, 1932, 26, 23.

<sup>50</sup> H. W. Starkweather, *J.A.C.S.*, 1934, 56, 1870.

<sup>51</sup> See W. H. Carothers, *Ind. Eng. Chem.*, 1934, 26, 30, and Chapter 8.

<sup>52</sup> For the polymerization of the light-ends of gasoline and the effect of these compounds on the viscosity index of lubricating oils see *Ind. Eng. Chem.*, 1935, 27, 7.

pressure caused the sample to become more gelatinous; ultimately a waxy gel was obtained which was somewhat drier than that obtained by ordinary heating.

One of the methods for following the course of a resin reaction of this type is the change in refractive index. During polymerization the unsaturation disappears and inasmuch as refraction is a function of unsaturation, a polymerization reaction would cause a lowering of the refractive index. Condensation reactions take place without the disappearance of unsaturation and no such lowering of the refractive index would be expected. Phenol-formaldehyde reactions are of the condensation type inasmuch as the refractive index increases with time. In styrene and tung oil the refractive index decreases.<sup>55</sup>

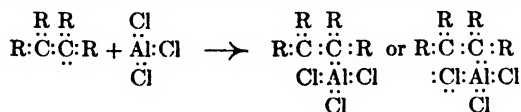
Katz<sup>54</sup> applied x-ray diffraction methods<sup>56</sup> to the study of polymerization. In many substances, styrene, indene, tung oil, isoprene, dimethylbutadiene, erythrene, the diameter of the diffraction ring was the same for the unpolymerized substance and for the polymerized derivative. On the other hand, ethyl cinnamate, methyl-ethylketone and methyl acrylate on polymerization showed considerable change in the diffraction pattern. Clark,<sup>56</sup> however, found that with tung oil an additional new ring of small diameter, that is, of large spacing, often appeared. Monomolecular dihydroxyacetone prepared by distillation of the dimolecular form was monomolecular as determined by cryoscopic measurements and gave a characteristic x-ray pattern. After the crystals had stood for several days, the diffraction pattern resembled that obtained by the dimolecular form even though molecular weight determinations still revealed only the monomolecular form.<sup>57</sup>

#### CATALYSIS OF ADDITION POLYMERIZATION

Catalysts exercise a profound effect on polymerization processes but their individual effect is not well understood. The more important catalysts for the polymerization of unsaturated compounds<sup>58</sup> include strong acids (sulphuric, hydrofluoric, phosphoric), anhydrous inorganic halides (aluminum chloride or bromide, ferric chloride, stannic chloride, antimony pentachloride), certain oxygenated substances (benzoyl peroxide, ozonides and oxygen) and highly absorbent materials (Florida earth, activated charcoal).

The effectiveness of a catalyst is assisted by heat to a certain extent depending on the stability of the polymer at any definite temperature. Catalysts lower the limit of stability, thus styrene undergoes the same polymerization in the cold in the presence of stannic chloride that it does at 270°C. by heat alone.<sup>59</sup>

The catalytic action of the inorganic halides is probably due to the ready formation of double compounds between the halides and the unsaturated substance undergoing polymerization. Hunter and Yohe<sup>60</sup> have suggested that an activated complex is formed in which one of the carbon atoms momentarily possesses a co-valency of three. Such a complex would be an excellent catalyst for polymeriza-



<sup>55</sup> R. Houwink, *Brit. Plastics*, 1934, 6, 100; *Brit. Chem. Abs.* B, 1934, 972.

<sup>54</sup> J. R. Katz, *Z. physik. Chem.*, 1927, 125, 321; *Brit. Chem. Abs.* A, 1927, 411. See *Z. angew. Chem.*, 1928, 41, 329; *Brit. Chem. Abs.* A, 1928, 464.

<sup>56</sup> For further use of x-rays see latter part of this chapter.

<sup>57</sup> G. L. Clark, *Nature*, 1927, 120, 119; *Brit. Chem. Abs.* A, 1927, 816.

<sup>58</sup> H. H. Strain and W. H. Dore, *J.A.C.S.*, 1934, 56, 2049.

<sup>59</sup> For a summary of these catalysts see H. Staudinger and H. A. Bruson, *Ann.*, 1926, 447, 110.

<sup>60</sup> H. Staudinger, *Ber.*, 1926, 59, 3031.

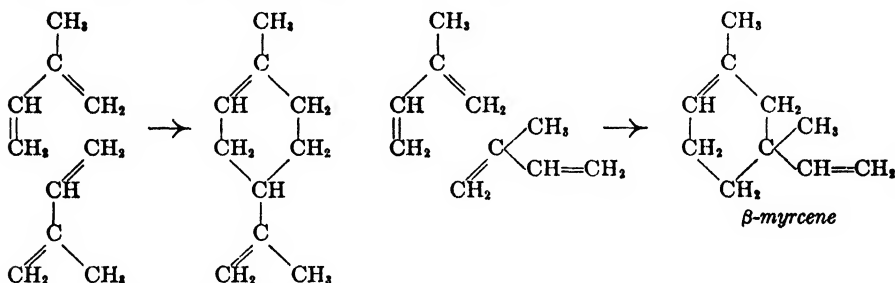
<sup>61</sup> W. H. Hunter and R. V. Yohe, *J.A.C.S.*, 1933, 55, 1248.

tion because it could immediately combine with another molecule of olefin. The new complex with a higher carbon content would still be in an activated state so that a long chain of carbon atoms might result by the interaction of incoming olefin molecules with those already present in the activated chain.

#### POLYMERIZATION OF THE DIOLEFINS

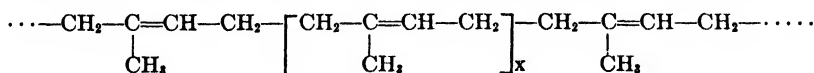
Of the diolefin hydrocarbons, those possessing a conjugated system of double bonds are of great interest because of their marked reactivity, polymerizing not only under the influence of heat but also with catalysts to yield substances of widely different properties.<sup>61</sup> Two types may be differentiated, the lower oily polymers of an unsaturated nature and macropolymers closely allied to rubber. (See Chapter 9.)

The lower oily polymers are usually cyclic hydrocarbons. Though unsaturated, the continued polymerization of these substances apparently does not result in the production of rubber-like polymers. This indicates that the unsaturated compounds can not be regarded as intermediates in the synthesis of the macropolymers. The dimers of the lower conjugated diolefins appear to be vinylcyclohexenes. Isoprene is known to yield at least two dimers



according to whether addition occurs to one or the other double bond of the isoprene.<sup>62</sup>

The formula assigned by Staudinger<sup>63</sup> to rubber is a linear structure of the type:



where the structural unit, or repeating pattern, is the active form of isoprene. On heating or by treatment with sulphuric acid, a cyclic product is supposed to be formed. This change is regarded as accounting for the alteration which occurs in rubber by treatment with vigorous reagents.<sup>64</sup>

Examination of unstretched rubber by x-rays reveals only an amorphous ring; stretched rubber, however, yields a sharp fiber diffraction pattern.<sup>65</sup> During the stretching process, rubber undergoes transformation from an amorphous to a crystalline state. This change is explained as follows: When rubber is stretched, the coiled chains pull out and cling together to yield long thin crystallites parallel to

<sup>61</sup> See E. N. Gapon, *J. Russ. Phys.-Chem. Soc.*, 1930, 62, 1385; *Brit. Chem. Abs. A*, 1931, 45, for a theoretical discussion of the polymerization of diethylenic compounds on the basis of a tervalent carbon. The energy necessary for this process represents the energy of activation.

<sup>62</sup> G. Egloff, M. Herrman, B. L. Levinson and M. F. Dull (*Chem. Rev.*, 1934, 14, 287) have reviewed the thermal reactions of isoprene and other terpene hydrocarbons.

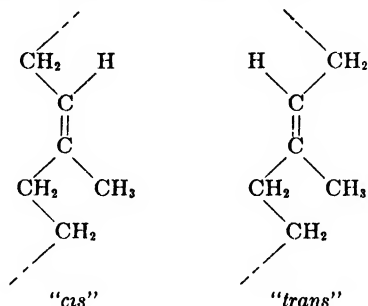
<sup>63</sup> H. Staudinger, "Die hochmolekularen organischen Verbindungen—Kautschuk und Cellulose." J. Springer, Berlin, 1932, 380. See Chapter 54.

<sup>64</sup> See Chapter 54.

<sup>65</sup> J. R. Katz, *Chem.-Ztg.*, 1925, 49, 353; *Chem. Abs.*, 1925, 19, 2144.

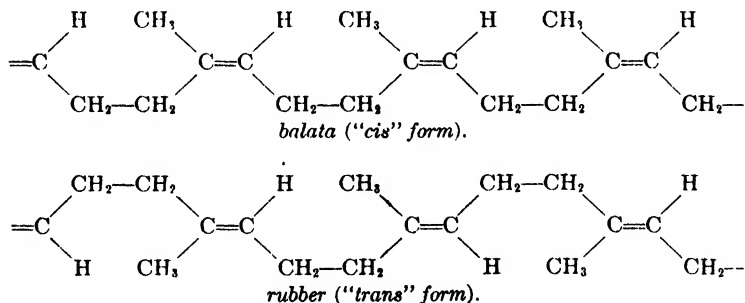
the direction of stretching and are analogous to the long thin crystallites of silk, cellulose and wool to be mentioned later.<sup>66</sup>

The presence of the double bond in rubber brings about the possibility of stereoisomerism not only of "cis" and "trans" forms but of both.



The data from x-rays favor the "cis" form.<sup>67</sup> A large model arranged in the "cis" form can be coiled up into a cylindrical spiral and this spiral can be stretched out into a long chain. Swelling in solvents is attributed to the effect of solvent molecules which force themselves between the turns of the spiral and become attached to residual valencies causing a lengthening of the main valency chain. Vulcanization effects a union between the rubber spiral chains by sulphur bridges. A large amount of sulphur, however, causes the structure to be rigidly linked together.<sup>68</sup>

Staudinger<sup>69</sup> considers rubber to be a trans compound and balata to be a cis-derivative.



Further differences occur between these two compounds other than the stereo-

<sup>66</sup> W. E. Singer, J. D. Long and W. P. Davey (*Physical Rev.*, 1933, (2) 44, 319; *Brit. Chem. Abs. B*, 1935, 153) have shown by means of x-ray diffraction studies that there is a time lag between the time rubber is stretched and the time the fiber structure is produced. The phenomenon of time lag has been explained on the basis that rubber consists of a tangle of spiral or "zig-zag"-shape molecules with firmly fixed ends, the lengths of which can be temporarily untangled by the application of an external force.

<sup>67</sup> E. Mack, (*J.A.C.S.*, 1934, 56, 2766) has discussed the various factors which influence "cis" and "trans" addition in the formation of rubber and gutta-percha.

<sup>68</sup> H. Fikentscher and H. Mark, *Kautschuk*, 1930, 6, 2; *Brit. Chem. Abs. B*, 1930, 249. See K. H. Meyer and H. Mark, *Ber.*, 1928, 61, 1939; *Brit. Chem. Abs. A*, 1928, 1252. Celluloid is a perfect analogy for rubber. In the unstretched condition the x-ray diffraction pattern yields an amorphous scattering due to the fact that the camphor swells up the nitrocellulose. On stretching the celluloid, the camphor is expelled from the fiber structure and the nitrocellulose pattern can again be obtained. See K. H. Ueda, *Z. physik. Chem.*, 1928, 133, 350; *Brit. Chem. Abs. A*, 1928, 818.

<sup>69</sup> H. Staudinger, *Kautschuk*, 1934, 10, 6. *I. R. I. Transactions*, W. Heffer and Sons, Ltd.; Cambridge, 1935, 10 (3), 263. See H. Staudinger and H. F. Bondy, *Ann.*, 1929, 468, 1; *Chem. Abs.*, 1929, 23, 3372. Cf. D. K. Memmler, "The Science of Rubber," trans. D. F. Dunbrook and V. N. Morris, Reinhold Publishing Corp., New York, 1934.

chemical arrangement; the molecular weight of balata is much smaller. Mastication of rubber results in a shortening of the molecule. The smaller molecular weight would account for both the increased solubility and decreased swelling of the masticated form. (See Table 5).

TABLE 5.—*Rubber and Balata.*

Compound	Number of Isoprene Units	Molecular Weight	Length of Molecule in Å.u
Rubber, benzene soluble.	1300	88,000	5800
Rubber, ether soluble	930	64,000	4200
Masticated rubber . .	300	20,000	1350
Balata . . . . .	590	40,000	2650
Decomposed balata	100	6,800	450

The molecular weights of rubber and balata and of masticated rubber agree in order of magnitude with the particle size deduced by osmosis.<sup>70</sup> It appears, therefore, that osmotic pressure determinations do not determine the micelle weight of rubber but actually the true molecular weight.

Rubber is particularly sensitive to oxygen. Staudinger considers that rubber decomposes according to the following reaction scheme:

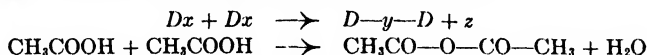


It can thus be readily seen that a very small quantity of oxygen can cause a great change in the physical properties. This reaction takes place in solution. In the solid state, however, the oxygen acts in such a way as to form oxygen bridges between the thread-like molecules.<sup>71</sup> Because of this action rubber of unlimited swelling capacity is converted into a rubber of limited swelling capacity. On this basis, the conversion of rubber from the soluble to the insoluble variety is therefore not a colloid chemical action but wholly a chemical action by which 3-dimensional macromolecules are formed from thread-like molecules.

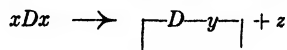
#### CONDENSATION REACTIONS

In a condensation reaction, the polymer is no longer a multiple of the monomer as in the case of the addition polymer. During the reaction no addition of the reactants occurs but simple molecules such as water, alcohol, hydracid, sodium chloride are eliminated. In the final condensate, therefore, it is necessary to subtract the sum of the atoms liberated in order to determine the structural formula.

Single condensations do not yield a substance with resinous properties. In order to build up a large molecule, the reacting molecule must have more than one grouping to allow a multicondensation to take place.



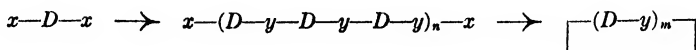
In this instance, a condensation has taken place but no polymer results. With two reacting groups, or as they are more usually termed, functional groups, several reactions may take place: 1) intramolecular condensation:



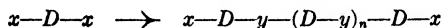
<sup>70</sup> W. A. Caspari, *J.C.S.*, 1914, 105, 2139. K. H. Meyer and H. Mark, *Ber.*, 1928, 61, 593. H. Kroeplin and W. Bumshagen, *Ber.*, 1928, 61, 2441. W. Ostwald, *Kolloid.-Z.*, 1929, 49, 60.

<sup>71</sup> See H. Staudinger and H. F. Bondy, *Ann.*, 1933, 488, 153. Cf. three-dimensional polymers in this chapter.

2) the reaction may be intermolecular to build up a long chain and then become intramolecular



or 3) the reaction may be wholly intermolecular and yield a linear polymer



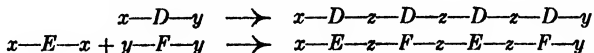
The question naturally arises as to just when intermolecular condensation takes place in preference to intramolecular condensation. Carothers<sup>73</sup> has developed a general rule to the effect that when the number of molecules in a unit chain is five, the product is monomeric and cyclic; if the number is six, the product may be either mono- or polymeric and if the number is greater than six, it is exclusively polymeric. In other words when stereochemically possible, cyclization will take place but this will only occur when the functional groups are very close together in the same molecule. When sufficiently separated, intermolecular reaction is to be expected.

This is at first difficult to reconcile with Ruzicka's<sup>74</sup> discovery that high-membered cyclic compounds can be prepared and are in no way less stable than smaller ones. That the rings are non-planar and strainless<sup>74</sup> can be seen on the basis of the Sachse-Mohr<sup>75</sup> theory inasmuch as there is a free rotation around each single bond in the chain; the 5-membered ring is planar and free from strain; the 6-membered ring is highly strained unless two of the atoms are on a different plane from the other four; larger-membered rings possess a marked mobility and can assume a multiplicity of shapes. X-Ray measurements reveal that these molecules contain double chains.<sup>76</sup>

These many-membered rings prepared by intramolecular reaction appear to be a peculiar phenomenon in that they are formed more through the accidental approach of the terminal groupings. The more general reaction is the intermolecular reaction.

#### TYPES OF MULTICONDENSATION

In the case of addition polymerization, it will be recalled, there were two types of addition: one the homo- and the other co-polymerization. Analogous types exist in multicondensation reactions, and they may be expressed as follows:



An example of the different types of condensation can be seen in the formation of polyesters. The hydroxyl and carboxyl group may exist in the same molecule and lead to a homo-condensation or the hydroxyl groups may exist in one molecule

<sup>73</sup> W. H. Carothers, *Chem. Reviews*, 1931, 8, 353.

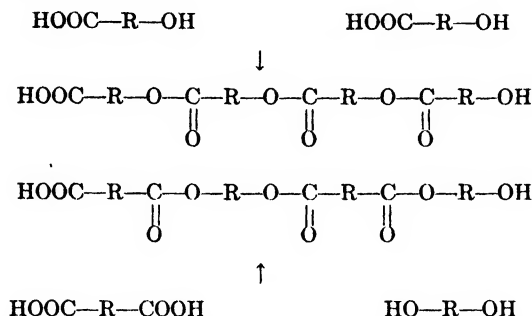
<sup>74</sup> For the formation of many-membered cyclic rings see L. Ruzicka et al., *Helv. Chim. Acta*, 1926, 9, 230, 249, 339, 389, 399, 499, 715, 1008; 1927, 10, 695; 1928, 11, 496, 670, 686, 1174, 1159. For a review see L. Ruzicka, *J.S.C.I.*, 1935, 54, 2.

<sup>75</sup> H. D. K. Drew (*J.S.C.I.*, 1933, 52, 538) draws attention to the fact that these large rings can form a plane structure.

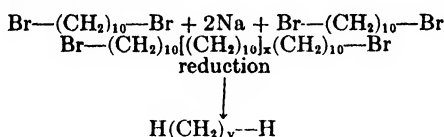
<sup>76</sup> E. Mohr, *J. prakt. Chem.*, 1918, 98, 315; *Chem. Abs.*, 1919, 13, 2661. See H. Sachse, *Ber.*, 1890, 23, 1363; *J.C.S.*, 1890, 58, 1396.

<sup>77</sup> A. Müller, *Helv. Chim. Acta*, 1933, 16, 155; *Brit. Chem. Abs. A*, 1933, 267. See also M. Stoll and G. Stolle-Comte, *Helv. Chim. Acta*, 1930, 13, 1185. J. R. Katz, *Z. angew. Chem.*, 1929, 42, 828.

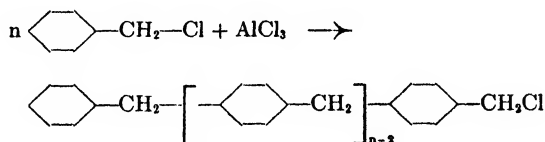
and the carboxyl groups in another. In both instances, esters will be formed but they will differ in arrangement.



Numerous other types of condensation-polymerization exist and these may be summarized as follows. Long chain paraffins can be built up by the action of sodium on the polymethylene bromides followed by reduction in order to replace the terminal halogens by hydrogen.<sup>77</sup>



A bi-functional Friedel and Crafts<sup>78</sup> reaction, leading to the formation of polymerized material, can be seen in the action of aluminum chloride on benzyl chloride:



Other reactions yielding linear polymers by condensation include formation of polyamides,<sup>79</sup> polyamines,<sup>80</sup> polyacetals,<sup>81</sup> polyanhydrides,<sup>82</sup> polymethylene sulphide iodides,<sup>83</sup> aniline black,<sup>84</sup> polyphenylene ethers<sup>85</sup> and many many others which will be discussed in the following chapters.

#### STRUCTURE OF POLYMERS

When the colloid chemist dealt with the so-called "bio-colloids," he used the empirical concepts of "particle size" and "micellar structure" and regarded molecular weights and molecular individuality with considerable skepticism. One of

<sup>77</sup> W. H. Carothers, J. W. Hill, J. E. Kirby and R. A. Jacobson, *J.A.C.S.*, 1930, 52, 5279. See also A. Franke and O. Kienberger, *Monat.*, 1912, 33, 1189; *Chem. Abs.*, 1913, 7, 587.

<sup>78</sup> C. Friedel and J. M. Crafts, *Bull. soc. chim.*, 1885, 43, 53. See C. K. Ingold and E. H. Ingold, *J.C.S.*, 1928, 2249. S. N. Ushakov and A. V. Kon, *Zhur Prikladnoi Khimii*, 1930, 3, 69; *Chem. Abs.*, 1930, 24, 3796.

<sup>79</sup> J. von Braun, *Ber.*, 1907, 40, 1835.

<sup>80</sup> J. von Braun, *ibid.*, 1910, 43, 2853.

<sup>81</sup> H. S. Hill and H. Hibbert, *J.A.C.S.*, 1923, 45, 3124.

<sup>82</sup> J. W. Hill, *J.A.C.S.*, 1930, 52, 4110. See Chapter 50.

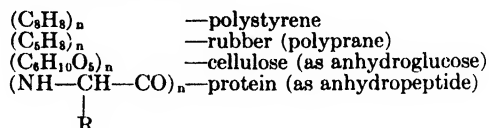
<sup>83</sup> J. von Braun, *Ber.*, 1910, 43, 3220.

<sup>84</sup> R. Willstätter and C. Cramer, *ibid.*, 1910, 43, 2976.

<sup>85</sup> S. Goldschmidt, E. Schulz and H. Bernard, *Ann.*, 1930, 478, 1.

the earlier explanations offered was that proposed by Ostwald<sup>86</sup> who observed that these high-molecular-weight substances went through physical changes akin to dispersoids and called them "isocolloids."<sup>87</sup> Krumbhaar,<sup>88</sup> Wolff,<sup>89</sup> Scheiber,<sup>90</sup> Auer<sup>91</sup> and Wornum<sup>92</sup> have used colloidal concepts in an attempt to explain the reactions which occur in drying oils.

The continued interest in such substances as rubber, resins, cellulose, cellulose derivatives, starches, proteins and also in the synthetic resins has brought divergent views concerning their structure. These derivatives can be represented very simply by the empirical formulas:



where "n" indicates not only an unknown magnitude but also an unknown quality or kind of aggregation by which the units are united.

At least three different concepts have been utilized in an attempt to explain the manner in which these basal or structural units are united. The first, with which Staudinger's<sup>93</sup> name is associated, is that the structural units are bound together by the primary valences of the orthodox organic chemistry. Opposed to this theory are those of Hess and Pringsheim<sup>94</sup> and of Bergmann.<sup>95</sup> They are known as the association and the co-ordination theories respectively. Hess and Pringsheim believe that the unit structures are monomeric or dimeric and are held together by secondary valence forces or by association. Bergmann's theory is that the structural unit is co-ordinated in the solid state and the unit, as such, is incapable of free existence in the vapor phase or in solution. Polysaccharides and proteins are thus built up of small units associated in the large molecules by supermolecular affinities similar to that of molecules in a crystal lattice. The structural unit, as in the crystal, loses its independence and individuality, as such, within the larger aggregate.

Following the establishment, by x-rays, of definite periodicity in such substances as rubber, cellulose,<sup>96</sup> polycyclopentadiene<sup>97</sup> and polyoxymethylene,<sup>98</sup> Mark and Meyer<sup>99</sup> proposed their "micellar" theory where the high molecular weight organic compounds are considered to be linked together into chains by primary valence forces. Bundles of these chains are associated laterally by secondary valences to form micelles which act as entities and are responsible for the colloidal properties.

No attempt will be made to evaluate the experimental results on which the

<sup>86</sup> W. Ostwald, "Handbook of Colloidal Chemistry," p. 103.

<sup>87</sup> See Chapter 3.

<sup>88</sup> Krumbhaar, *Chem.-Ztg.*, 1916, 40, 937; *Chem. Abs.*, 1917, 11, 1314

<sup>89</sup> H. Wolff, *Farben. Ztg.*, 1926, 31, 1239, 1457, *Chem. Abs.*, 1927, 21, 1716

<sup>90</sup> J. Scheiber, *Farbe u. Lack*, 1927, 75, 135; *Chem. Abs.*, 1928, 22, 3054

<sup>91</sup> L. Auer, *Chem. Umschau Fette Oele Wachse Harze*, 1928, 35, 9, 27; *Chem. Abs.*, 1928, 22, 1695

<sup>92</sup> W. E. Wornum, *J. Oil, Colour Chem. Assoc.*, 1934, 17, 119, *Chem. Abs.*, 1934, 28, 3915

<sup>93</sup> H. Staudinger, "Die hochmolekularen organischen Verbindungen" See also H. Staudinger, *Int. Intern. chim. Solvay, Conseil chim., 4th Conseil, Brussels*, 1931, 101; *Chem. Abs.*, 1933, 27, 948. *Kolloid-Z.*, 1930, 53, 19. *Helv. Chim. Acta*, 1930, 12, 1183. *Naturwissenschaft*, 1934, 22, 65, 84. H. Staudinger and W. Heuer, *Z. physik. Chem.*, 1934, 171, 129. For criticism of K. Meyer and H. Mark's theory (*Ber.*, 1931, 64, 1999, *Brit. Chem. Abs. A*, 1931, 1276) see H. Staudinger, *Ber.*, 1931, 64, 2721.

<sup>94</sup> H. Pringsheim, *Naturwissenschaft*, 1924, 12, 360; *Chem. Abs.*, 1924, 18, 2331. K. Hess, *ibid.*, 1926, 14, 435; *Chem. Abs.*, 1926, 20, 2410

<sup>95</sup> M. Bergmann, *Z. angew. Chem.*, 1925, 38, 1141; *Chem. Abs.*, 1926, 20, 2684. *Ber.*, 1926, 59, 2973.

<sup>96</sup> See G. L. Clark, "Applied X-Rays," McGraw-Hill Book Co., Inc., New York, 1932, and *Ind. Eng. Chem.*, 1929, 21, 128. See also E. A. Hauser, *ibid.*, 124.

<sup>97</sup> J. Hengstenberg, *Ann.*, 1928, 467, 91; *Chem. Abs.*, 1929, 23, 1625

<sup>98</sup> J. Hengstenberg, *Ann. physik. Chem.*, 1927, 84, 245; *Chem. Abs.*, 1928, 22, 728. E. Ott, *Helv. Chim. Acta*, 1928, 11, 300; *Chem. Abs.*, 1928, 22, 1879.

<sup>99</sup> H. Mark and K. H. Meyer, *Ber.*, 1928, 61, 593. See also "Die Aufbau der hochpolymeren organischen Naturstoffe," Akad. Verlagsges. m. b. H., Leipzig, 1930.



individual theories have been based. Consideration will be given, however, to the primary valence theory inasmuch as it appears useful in predicting properties.

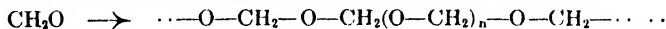
According to Staudinger the molecules are long thread-like chains of the monomeric groups linked together by primary valence bonds. As the degree of polymerization becomes greater, the molecular weight increases and the length of the chain likewise increases. The chain is in effect a single molecule and the properties of the polymer depend on the length of the chain. When the length of the chain is relatively short, hemi-colloids are obtained. Longer chains lead to "eucolloidal" properties.

In hemi-colloids, the mean molecular weight varies from 2000-10,000 and the single molecule consists of approximately 50-100 monomeric units. It is to be understood of course that in no instance are the chains in any one product of the same length, consequently both the molecular weight and the number of structural units must be an average figure. Solutions of hemi-colloids show relatively low viscosity and after the solution has been heated, the viscosity is not materially altered. The thermal softening point of the hemi-colloid is relatively low and the substance tends to be precipitated as an amorphous powder from solution upon addition of a nonsolvent.

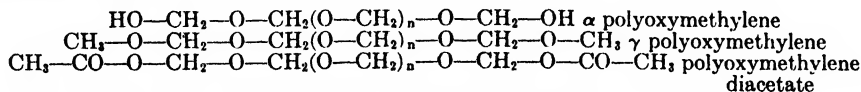
Eucolloids<sup>100</sup> consist of molecules which are much longer than those of hemi-colloids. The mean molecular weight varies from 10,000 to well above 100,000 and the chain may consist of as many as 3000 monomeric units. The thermal softening point of the eucolloid is high and the substance, in contrast to hemi-colloids, is precipitated from solution as a material of a more or less fibrous nature. In solution, eucolloids have a high viscosity—a property which may be lowered by heat treatment. At the higher temperature, the longer chains are unstable and decompose into somewhat shorter ones.

When eucolloids do form, they are the end-products of a reaction which has taken place at a relatively low temperature. The lower the temperature, the greater tendency there is for the formation of the eucolloid. This is because the chain is sensitive to heat and the higher the temperature the shorter the chain.<sup>101</sup> Catalysts have the same effect as increase in temperature; rapid polymerization produces the hemi-colloid; slow polymerization yields the eucolloid.<sup>102</sup>

The polymerization of unsaturated compounds to a long thread-like chain leaves the end groups unsaturated:

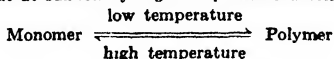


These ends are troublesome to account for and various methods have been suggested to overcome the anomalously resulting structure. Conceivably the free radicals may be oxidized or otherwise converted to saturated groupings or the ends may combine with the molecules of the solvent.



<sup>100</sup> H. Staudinger (*Ber.*, 1934, 67, 1255) discusses the origin of the term "eucolloid."

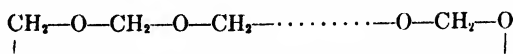
<sup>101</sup> It is usually considered that at sufficiently high temperature decomposition to the monomer results.



There is a question, however, as to whether this is always true. F. O. Rice and K. K. Rice have recently reviewed the manner in which the various high polymers would be expected to behave on decomposition. See "The Aliphatic Free Radicals," The Johns Hopkins Press, Baltimore, 1935, 142 seq.

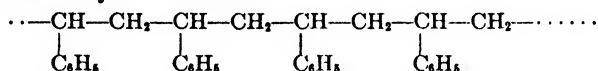
<sup>102</sup> W. H. Carothers and J. W. Hill (*J.A.C.S.*, 1932, 54, 1587) found that the linear polyesters in spite of the high molecular weights are formed at 200-250°C. and show no sign of being degraded by repeated exposure to high temperatures.

Moreover, the free ends might combine intramolecularly to form rings.

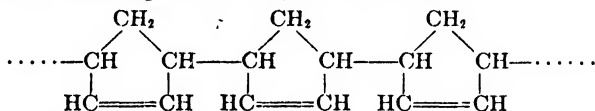


Carothers,<sup>108</sup> however, does not consider such large ring structures feasible. In any polymerization, be it condensation or addition, the reaction must be step-wise and consequently ring closure if it is to take place must occur as the last step in the reaction. The longer the chain, however, the more distant the ends must be and the less opportunity there is for ring closure.

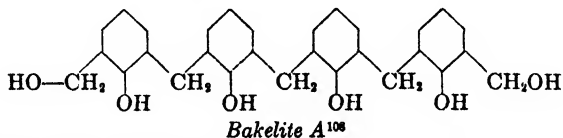
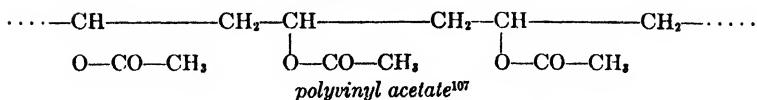
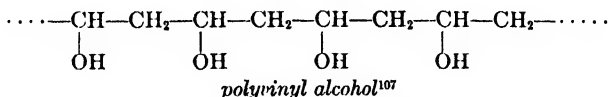
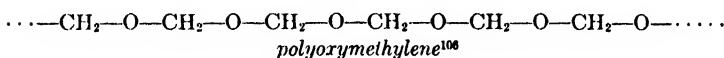
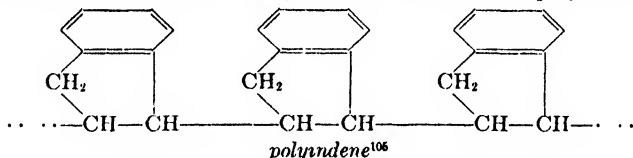
The relation between the solubility and the length of chain is not easily discernible. Some molecular chains of great length are soluble whereas others of relatively short length are insoluble. Polystyrene, consisting of perhaps a thousand structural units is soluble but one form of polycyclopentadiene, containing 6 pentadiene units per molecule is insoluble. Polystyrene consists of a long saturated chain with phenyl groups hung along this chain at each alternate carbon and tends to form only linear chains



Polycyclopentadiene<sup>104</sup> may undergo secondary polymerization between the remaining double bonds resulting in an irregular molecule



Linear structures have been suggested for other macropolymers:



<sup>108</sup> W. H. Carothers, *Chem. Reviews*, 1931, 8, 379.

<sup>104</sup> See Chapter 9 for another version of the structure of polymerized cyclopentadiene.

<sup>106</sup> H. Staudinger, A. A. Ashdown, M. Brunner, H. A. Bruson and S. Wehrli, *Helv. Chim. Acta*, 1929, 12, 984.

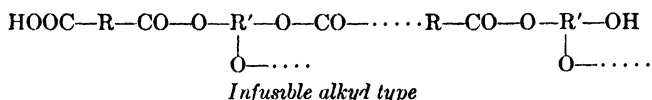
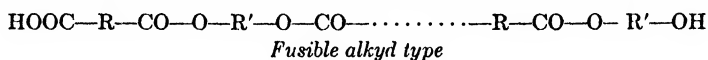
<sup>108</sup> H. Staudinger, R. Signer, H. Johner, M. Lüthy, W. Kern, D. Russidis and O. Schweitzer, *Ann.*, 1929, 474, 145.

<sup>107</sup> H. Staudinger, K. Frey and W. Starck, *Ber.*, 1927, 60, 1782.

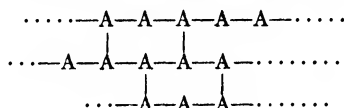
<sup>109</sup> A. E. Blumfeldt, *Chem.-Ztg.*, 1929, 53, 493. See Chapter 14.

### THREE-DIMENSIONAL POLYMERS

The distinct illustration of the possible relation between chemical structure and solubility is shown in the glycol and glycerol phthalates. Glycol phthalate can form only linear polyesters by multicondensation and tends to remain soluble in all stages.<sup>109</sup> Glycerol phthalate, on the other hand, can grow in more than one direction and as the size of the molecule becomes greater, it also becomes more complex and compact with the result that the solubility and fusibility decrease.



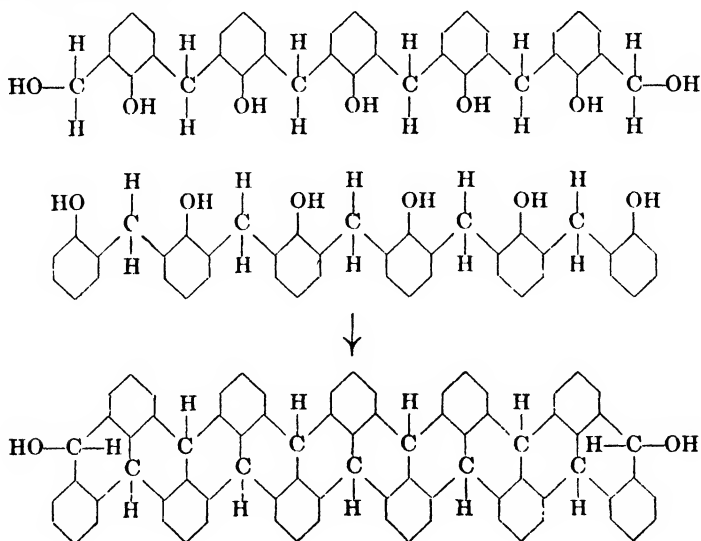
Moreover, wherever a double bond or other sensitive point occurs in the chain, the tendency is toward the formation of insoluble products. This apparently is due to cross-linkages between the chains. If "A" represents a monomeric group containing a double bond or other sensitive group, the action may be expressed:

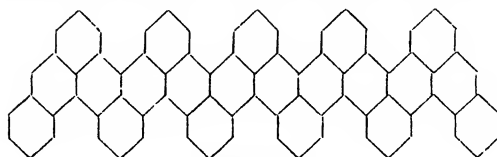


For example one may consider two molecules of Bakelite A yielding the insoluble and infusible Bakelite C.<sup>110</sup>

<sup>109</sup> See Chapter 41 and *seq.*

<sup>110</sup> On the following page is given the manner in which A. E. Blumfeldt (*loc. cit.*) represents the formula giving the impression that the molecule is aromatic. Actually the compound as worked out on his basis is hydraromatic, and also contains terminal hydroxyl groups. M. Koebner (*Chem.-Ztg.*, 1930, 54, 619; *Chem. Abs.*, 1930, 24, 6039) has criticized Blumfeldt's formula because it fails to account for the presence of hydroxyl groups.





Bakelite C.

Cross-linkage of molecular chains can be accomplished through the addition of other reagents. Resins of this type are known as element-convertible and include blown oils, olefin-sulphur resins and the unsaturated acid-modified glycerol-polybasic acid resins. See Table 6.

Certain other features distinguish the linear from the three-dimensional polymer. The 2, 2<sup>111</sup> type of polymer (cellulose, rubber, polyoxymethylene, glycol-polyesters) on x-ray examination reveals a pseudo-crystalline or fibrous structure whereas the 2, 3 (or greater) type of polymer (glycerol phthalate, Bakelite) reveals more of the amorphous structure.<sup>112</sup>

TABLE 6.—*Synthetic Resins and Their Polymers* \*

Reacting Molecules	Reactivity	Preparation	Length of Chains	Mol. wt.	Type Resin
Styrene.....	2 2	Heat	Long	Very high	Non-convertible
Formaldehyde.....	2 2	Heat	Long	Very high	Non-convertible
Cyclopentadiene.....	2 2	Heat	Long	High	Non-convertible
Phenol-aldehyde.....	2 2	—H <sub>2</sub> O (acid)	Long		Non-convertible
Glycol phthalic anhy....	2 2	—H <sub>2</sub> O	Long	High	Non-convertible
Phenol-aldehyde....	4 2	—H <sub>2</sub> O	Short	Moderate	Convertible
Glycerol phthalic anhy. .	3 2	—H <sub>2</sub> O	Short twining	Moderate	Convertible
Cyclopentadiene . . . .	4 4	Heat pressure	Short twining	Moderate	Convertible
Drying oil oxygen....	(6-8) 2	Heat pressure	Short twining	Moderate	Convertible

\* R. H. Kienle, *Ind. Eng. Chem.*, 1930 22, 592.

Moreover certain correlations may tentatively be made between the distances between the reactive groups which are involved in cross-linkages and in the hardness of the resin.<sup>113</sup> If the distance between the reactive groups is great, that is, there are many saturated points between them, the cross-linkages must of necessity be widely apart; consequently the macromolecule will tend to be of an open structure and will be soft and possess a low melting point. The more rigid and compact the molecule is, due to many cross-linkages, the higher will be the melting point. The concept has been offered as an explanation for the hardness of phthalate resins as compared with citrate resins of the alkyd type. The glycol phthalate resins exhibit a similar phenomenon; ethylene glycol (HO-CH<sub>2</sub>-CH<sub>2</sub>-OH)

<sup>111</sup> The 2,2 type of polymer is one in which only two functional groups react to form a polymer. Thus in the case of the glycol polyesters, there are two reactive groupings in glycol (HO-CH<sub>2</sub>-CH<sub>2</sub>-OH) and two reacting groupings in the acid (HOOC-R-COOH). When glycol reacts with a dibasic acid, molecular growth can only occur in one direction and only a linear polymer can result. Glycerol, however, containing three hydroxyl groups, can grow in other directions than in the linear form. In other words, the functional activity of glycerol is three.

Cellulose is considered as a 2,2 polymer even though the glucopyranose from which it is derived has a functional reactivity of 5. Only two of the five functional groups are involved in the formation of the polymer.

<sup>112</sup> See R. H. Kienle, *Ind. Eng. Chem.*, 1930, 22, 592. For further discussion, see latter part of this Chapter.

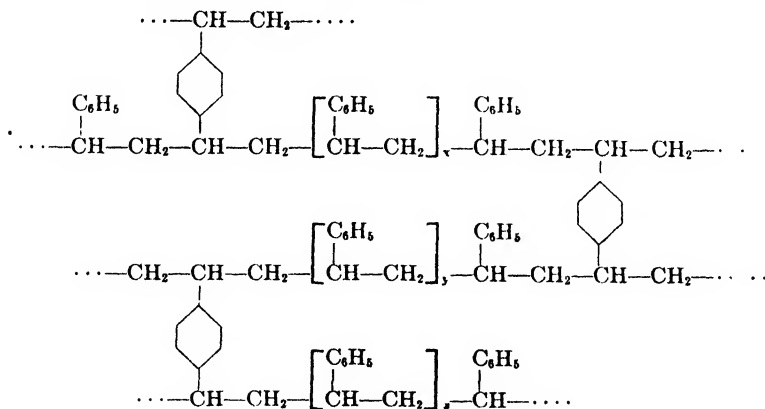
<sup>113</sup> N. Tsonev and N. Yavnel (*Masloboina Zhirovoe Delo*, 1932 (9), 28; *Chem. Abs.*, 1933, 27, 3471) have suggested that the hardest resins are obtained from the least symmetrical molecules. Cf. Chapter 24.

forms a hard glassy resin; propylene glycol ( $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ ) yields a product which is less hard and possesses a lower melting point; whereas diethylene glycol ( $\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ ) gives rise to a product of balsam-like properties.<sup>114</sup>

Essentially the same relation exists in the condensation products of aminoaryl-sulphonamides and aldehydes.<sup>115</sup> Hardenability depends not so much on molecular magnitude as upon the constitution of the resin with respect to ring closure and cross-linkages. Hardenability is not observed in the aminoarylsulphonamide condensation product with formaldehyde, even when the number of amino groups is sufficient for the purpose, if either one or the other amino group does not react with the aldehyde or if molecular association is impeded at one of the two positions. Excessive spatial proximity of the reactive groups (e.g., in the ortho position) is a barrier to reactivity. The primary condensation may take place but the second group does not react. Depending on the initial starting material and the choice of reaction conditions aniline mono- or polysulphonamides can be made to yield crystalline compounds or resins which belong to the fusible or infusible type. Condensations with benzaldehyde yielded crystalline derivatives; acetaldehyde and furfural gave rise to crystalline compounds or infusible resins whereas formaldehyde gave rise to all three varieties.<sup>116</sup>

From evidence obtained in glycerol-phthalic anhydride condensation and in the tung oil polymerization, Wornum<sup>117</sup> believes that at low temperature straight-chain reaction occurs to form a small number of large units. Under these conditions gelation occurs only upon long heating. At high temperature 3-dimensional growth occurs immediately, yielding a large number of small units. Cross-linkages occur rapidly, bringing about phase complexity and gelation. It appears that at low temperature the  $\beta$ -hydroxyl group is inactive and only the  $\alpha$ -hydroxyl groups react, consequently a linear polymer is obtained. At higher temperatures all three hydroxyl groups enter into the reaction.

A somewhat analogous situation exists when styrene and divinylbenzene are allowed to polymerize.<sup>118</sup> Styrene, as has been mentioned, gives rise to a linear polymer. Divinylbenzene, having two vinyl groups can build up a 3-dimensional polymer. Combination of styrene and divinylbenzene yields a compound whose general structure may be represented as follows:



<sup>114</sup> L. A. Jordan and J. O. Cutter, *J.S.C.I.*, 1935, 54, 89T.

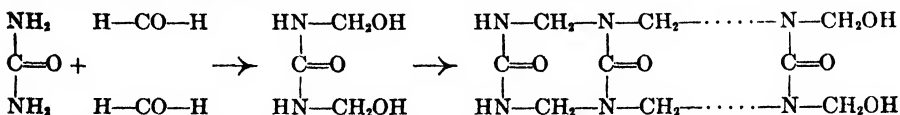
<sup>115</sup> See Chapter 34.

<sup>116</sup> G. Walter and H. Pollak, *Kolloid-Beihfte*, 1934, 40, 1; *Brit. Chem. Abs. B*, 1934, 1020.

<sup>117</sup> W. E. Wornum, *J. Oil, Colour Chem. Assoc.*, 1933, 16, 231.

<sup>118</sup> H. Staudinger, *Kautschuk*, 1934, 10, 7.

The reaction between urea and formaldehyde may be considered to give rise to a 3-dimensional polymer.<sup>119</sup>



Houwink<sup>120</sup> has compared the gelatin gel with the urea-formaldehyde condensation product in its initial stages of formation. Both substances contain large amounts of water and form strongly lyophilic masses. Following the supposed reaction mechanism it can be seen how the presence of the hydroxyl groups in the dimethylolurea might be responsible for the hydrophilic properties of the gel. On heating and elimination of water with the formation of macromolecules, the hydroxyl groups would disappear with a corresponding reduction of the hydrophilic properties.

### NATURAL PRODUCTS

These linear polymeric representations of synthetic materials have lent definite support to similar structures assigned to natural products. This has already been partly shown in the case of rubber. Other natural products which have been analogously treated are cellulose, wool, silk and other proteins. As evidence continues to accumulate, there appears to be a most intimate relation between resins, rubber-like products and fiber structures.

Much of the work which has been carried out on rubber and on fibrous structures is of immense importance in the field of synthetic resins. Rubber at low temperatures is hard and brittle and it may be that rubber owes its chief virtue to the fortuitous circumstance of having elastic properties at room temperature. At high temperatures, rubber on treatment with air can be converted into a resin.<sup>121</sup> On the other extreme certain of the high-melting resins approach at high temperature the rubber-like state. Autopolymerized styrene behaves like raw rubber above 65°C.<sup>122</sup> Above this temperature, the styrene polymer may be "racked."<sup>123</sup>

Von Weimarn<sup>124</sup> has called attention to the fact that linear polymers such as rubber, silk, resins, lacs, lubricating oils and the like may exist in the mesomorphic state of matter.<sup>125</sup> According to Friedel,<sup>126</sup> there are sharp discontinuities between the liquid (amorphous phase), the nematic state (where the long molecules point in one direction but are not grouped into parallel planes), the smectic state (where the molecules are arranged in parallel planes) and the crystalline state (where the molecules are marshalled into a 3-dimensional pattern). An experiment of de Jong<sup>127</sup> is of interest in this connection. A thin film of gutta-percha hydrocarbon, obtained by slow evaporation of a benzene solution, consisted in microscopic rosettes of needles. After stretching, this film showed straight extinction with polarized light between crossed Nicol prisms.

<sup>119</sup> See Chapter 26.

<sup>120</sup> R. Houwink, "Physikalische Eigenschaften und Feinbau von Natur- und Kunstharnen," Leipzig. Akad. Verlagsges.m.b.H., 1934. "British Plastics Year Book," 1935, Plastics Press, Ltd., London.

<sup>121</sup> A. Davies, British P 373,228, 1931; *Brit. Chem. Abs. B*, 1932, 739.

<sup>122</sup> G. S. Whitby, J. G. McNally and W. Gallay, "Colloid Symposium Monograph," Chemical Catalog Co., New York, 1928, 6, 232.

<sup>123</sup> For "racked" rubber, i.e., rubber which has been stretched and held rigid by excessive cooling under stress, see W. A. Gibbons, R. H. Gerke and H. C. Tingey, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 281.

<sup>124</sup> P. P. von Weimarn, "On the Rubber-Like and Liquid-Crystalline States of Matter," in J. Alexander's "Colloid Chemistry," Chemical Catalog Co., New York, 1931, 3, 89.

<sup>125</sup> Cf. experiments of D. Vörländer reported earlier in this chapter.

<sup>126</sup> G. Friedel, "The Mesomorphic States of Matter," in J. Alexander's "Colloid Chemistry," Chemical Catalog Co., New York, 1926, 1, 102.

<sup>127</sup> A. W. K. de Jong, *Rec. trav. chim.*, 1931, 50, 1011; *Brit. Chem. Abs. A*, 1931, 1421.

Another development is again due to von Weimarn.<sup>128</sup> He has succeeded in obtaining an unstable rubber-like substance from elementary sulphur. By pouring hot liquid sulphur at 400°C. in a thin stream into liquid air, solid and brittle threads are obtained; on warming, the threads acquire a high elasticity similar to that of rubber but the property disappears after a short time whereupon the sulphur becomes translucent and changes over to the normal viscous state.

Due to the rapid temperature drop of approximately 600°, some of the molecules become orientated whereas others form a highly disperse glass. As the temperature rises, the glass melts into a viscous liquid, yielding a system with the highly elastic properties of rubber.

Just what exact relation exists between fibers, resins and rubber is at present hypothetical. Resins may be an indiscriminate mixture of rod forms without any special attraction or repulsion in any one direction. In the case of fibers these same rods might be arranged parallel with attractive forces at the ends of the rod whereas in elastic substances there could be repulsive forces at the end of the chain so that they would attach themselves at right angles to one another. In such a state any deformation would cause the substance to return to its undeformed condition.<sup>129</sup>

#### CELLULOSE

The old micellar theory of von Nägeli<sup>130</sup> had postulated that in the cellulose fiber there were linear anisotropic micelles. Each individual micelle should behave as a small crystal. The theory was not accepted seriously. A great many years later, Ambronn<sup>131</sup> pointed out that, if cellulose were crystalline, it should reveal an x-ray pattern. His own studies on the accidental double refraction in celloidin (nitrocellulose) and in cellulose had indicated to him the essential truth of von Nägeli's theory of crystalline micelles. The strong dichroism shown by the natural fibers as well as by the permanently stretched celloidin appeared to be additional evidence.<sup>132</sup>

Both Scherrer<sup>133</sup> and Herzog and Jancke<sup>134</sup> almost simultaneously showed by x-ray patterns that cellulose was crystalline. Cotton, ramie, wood, artificial silk and viscose all revealed these patterns, moreover wood behaved similarly to cotton and ramie (see Fig. 5). It was further determined that the crystallites were parallel to one another and parallel to the crystallographic axis of the fiber.<sup>135</sup> Sponsler and Dore<sup>136</sup> then postulated the long chain structure for cellulose which together with the x-ray studies by Mark and Meyer<sup>137</sup> and Haworth's<sup>138</sup> proof of the structure of cellobiose and the relationships existing between glucose, cellobiose and cellulose have placed the polymeric linear structure beyond the hypothetical stage. Cellulose may now be considered to be built up of anhydroglucopyranoses as follows:

<sup>128</sup> P. P. von Weimarn, *Z. Chem. Ind. Coll.*, 1910, 6, 250; *Chem. Abs.*, 1910, 4, 2078.

<sup>129</sup> See G. Dring, *J.S.C.I.*, 1934, 53, 422.

<sup>130</sup> K. von Nägeli, "Pflanzenphysiologischen Untersuchungen," Zurich, 1858.

<sup>131</sup> H. Ambronn, *Kolloid-Z.*, 1917, 20, 173.

<sup>132</sup> H. Ambronn, *Nachr. Ges. Wiss. Göttingen, Mathphysik. Klasse*, 1919, 299; *Chem. Abs.*, 1921, 15, 3393. *Kolloid-Z.*, Special No., Apr. 1, 1925, 119; *Chem. Abs.*, 1925, 19, 2877. See Chapter 3.

<sup>133</sup> P. Scherrer, *Nachr. Ges. Wiss. Göttingen*, 1918, 96; *J.C.S.*, 1919, 116 (2), 274.

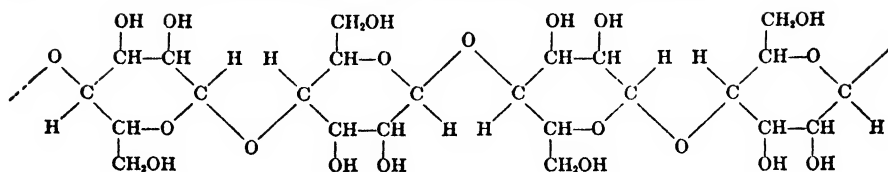
<sup>134</sup> R. O. Herzog and W. Jancke, *Z. angew. Chem.*, 1921, 34, 385.

<sup>135</sup> K. Bedou, R. O. Herzog, W. Jancke and M. Polyani, *Z. physik.*, 1921, 5, 61. R. O. Herzog, *ibid.*, 1920, 3, 96. *Z. angew. Chem.*, 1921, 34, 385. M. Polyani, *Z. physik.*, 1921, 7, 149.

<sup>136</sup> O. L. Sponsler and W. H. Dore, "Colloid Symposium Monograph," Chemical Catalog Co., New York, 1925.

<sup>137</sup> H. Mark and K. H. Meyer, *Ber.*, 1928, 61, 593.

<sup>138</sup> W. N. Haworth, C. W. Long and J. H. G. Plant, *J.C.S.*, 1927, 2809. Cf. also J. C. Irvine and E. L. Hirst, *J.C.S.*, 1922, 121, 1585.



There is considerable disagreement as to the number of glucose units in the chain. Meyer and Mark<sup>139</sup> estimate that the number is from 60-100 (i.e., molecular weight from 10,000-16,000). Staudinger<sup>140</sup> is disposed to set the molecular weight much higher. Stamm,<sup>141</sup> however, by means of the ultracentrifugal method,<sup>142</sup> studied the nature of pure cotton linters ( $\alpha$ -cellulose) in cuprammonium solvent and obtained a value, on a copper-free basis of  $40,000 \pm 5000$ , indicating that the cellulose molecule is built up of 200-260 simple glucose units.

Haworth and Machemer<sup>143</sup> determined the length of the cellulose chain by strictly chemical means, namely by estimating the terminal groups. By completely methylating cellulose the end groups of the product should be tetramethylated whereas the glucose units in the chain would be trimethylated. On hydrolysis, one of the terminal groups would be isolated as a tetramethylglucopyranose, the other terminal group would be hydrolyzed into 2, 3, 6-trimethyl glucose and methyl alcohol. From the ratio of the trimethyl to the tetramethylated products it was possible to estimate the length of the cellulose chain. It was found by this means that cellulose consisted of not less than 100 and not more than 200  $\beta$ -glucose units. This corresponds to a molecular weight of 20,000-40,000 or a mean value of approximately 30,000.

The most widespread views concerning the structure of cellulose have been developed on the one hand by Staudinger and by Meyer on the other. Staudinger<sup>144</sup> undertakes to show that certain structural units under the influence of co-valencies align themselves in one direction to form a fiber-like structure. Meyer<sup>145</sup> believes that these linear polymers unite to form a bundle, or micelle, by means of reciprocal lateral attraction. Other materials than cellulose can participate in the formation of this bundle so that a "mixed micelle" comparable to a mixed crystal can develop.

There are two general types of reaction which cellulose can undergo and these have been called the "micellar surface" and the "permutoid" reactions. These reactions appear to depend on whether the reagent penetrates between the micelles without attacking the internal structure or whether the reagent penetrates the whole structure attacking specific chemical groupings at each point of the lattice.<sup>146</sup>

Although a large and definite part of the cellulose fiber is crystalline, there is a certain amount of amorphous material in the fibers and in other cellulose products such as ramie, hemp, sisal, jute, flax, cotton and wood.<sup>147</sup> (See Figs. 5 and 6.) The

<sup>139</sup> K. H. Meyer and H. Mark, *Ber.*, 1928, 61, 593. See also H. Mark and K. H. Meyer, *Z. physik. Chem., Abt. B*, 1929, 2, 1929. H. Mark and G. v. Susich, *ibid.*, 1929, 4, 431.

<sup>140</sup> H. Staudinger and O. Schweitzer, *Ber.*, 1930, 63, 2317, 3122. H. Staudinger and H. Freunderberger, *ibid.*, 2331. See also H. Staudinger, *Naturwissenschaften*, 1934, 22, 797, 813.

<sup>141</sup> A. J. Stamm, *J.A.C.S.*, 1930, 52, 3047. For the determination of starch by the ultracentrifugal method see O. Lamm, *Kolloid.-Z.*, 1934, 69, 44; *Brit. Chem. Abs. A*, 1934, 1172.

<sup>142</sup> See the latter part of this chapter.

<sup>143</sup> W. N. Haworth and H. Machemer, *J.C.S.*, 1932, 2270.

<sup>144</sup> H. Staudinger, *Z. angew. Chem.*, 1929, 42, 37.

<sup>145</sup> K. H. Meyer, *Biochem. Z.*, 1929, 208, 1.

<sup>146</sup> H. Mark and K. H. Meyer, *Z. physik. Chem.*, 1929, (B), 4, 190; *Brit. Chem. Abs. A*, 1930, 280.

<sup>147</sup> R. Thiesen (*Ind. Eng. Chem.*, 1932, 24, 1032) in a study of natural products by means of the Spierer lens has found that cotton and ramie are built up of micelles in characteristic arrangement. In semi-rotten wood, the cells are similar in arrangement but stand out more clearly than in decayed wood. The transition stages which occur between sound wood and semi-rotten wood indicate a close relationship between cellulose and lignin.



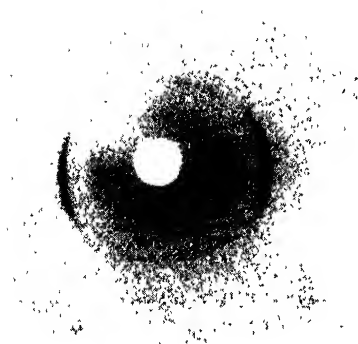


FIG. 5A.—  
X-ray Diagram of Native Cotton  
Cellulose.

FIG. 5B.—  
X-ray Diagram of Parana Pine  
Wood.

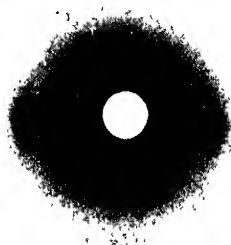


FIG. 6.—  
X-ray Diagram of Mercerized Ramie.

*Courtesy C. V. Holmberg and Prof. Louis E. Wise,  
Institute of Paper Chemistry, Appleton, Wis.*

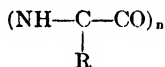
amorphous materials which may consist of resins, hemicelluloses and lignin do not interfere with the x-ray pattern. The crystalline part may be mercerized, nitrated, acetylated and treated chemically in the solid form and the resulting product is still a fiber crystal.<sup>148</sup>

According to von Weimarn,<sup>149</sup> it is possible to reduce cellulose to a plastic gel by treatment with aqueous saline solutions under appropriate conditions of pressure, temperature and concentration depending on the type of salt employed. Two extreme types of cellulose solution exist: (1) solutions containing elastic continuous jellies and (2) solutions failing to produce any aggregatory effect, or yielding precipitates. Between these types various intermediates exist. Cellulose jellies which have been washed to remove salts shrink rather rapidly, become denser and acquire considerable tensile strength. When completely dried, the jelly becomes brittle but preserves its tensile strength. The transition of cellulose jellies to plastics (in this case ointment-like masses) is dependent upon the concentration of products of cellulose hydrolysis in the gels. Beyond a certain concentration of such products, the properties of the jellies change from elastic systems into the region of plastic masses.

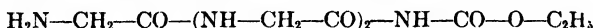
When cellulose is gelatinized in sodium hydroxide solution, heat is evolved; the amount increases with the concentration of caustic alkali.<sup>150</sup> The elasticity of these swollen fibers is comparable to that of rubber.<sup>151</sup>

### PROTEINS

The  $\alpha$ -amino acids, as is well known, are obtained by hydrolysis of proteins. These  $\alpha$ -amino acids contain bi-functional groups and would be expected to be linked up in the protein molecule as linear polymers, with the structural unit as the anhydro-amino acid.



Several of these reactions are known to occur. Glycine on heating in glycerol at 150-170°C. for 24-30 hours yields an amorphous polymer of the formula  $(\text{C}_2\text{H}_4\text{ON})$  which is reconverted to glycine by hydrolysis.<sup>152</sup> Moreover, glycine ethyl ester decomposes spontaneously, yielding glycol anhydride containing 4 unit groupings.<sup>153</sup> This reaction product may be expressed as:



Fischer's<sup>154</sup> famous synthesis of the octadecapeptide, l-leucyl-triglycyl-l-leucyl-triglycyl-l-leucyl-octaglycyl-glycine gave rise to a linear chain polymer of the same type:

<sup>148</sup> See G. L. Clark, *Ind. Eng. Chem.*, 1930, 22, 479. W. A. Sisson, *ibid.*, 1935, 27, 51. W. A. Sisson and G. L. Clark, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 296. See also G. L. Clark, "The Macromolecule and Micelle as Structural Units in Biological Materials with special reference to Cellulose," Cold Harbor Symposium on Qualitative Biology, Cold Spring Harbor, Biological Laboratory, 1964, 11, 28.

<sup>149</sup> P. P. von Weimarn, *Reports Imp. Ind. Research Inst., Osaka, Japan*, 1925, 5 (18), 7; *Chem. Abs.*, 1925, 19, 3568.

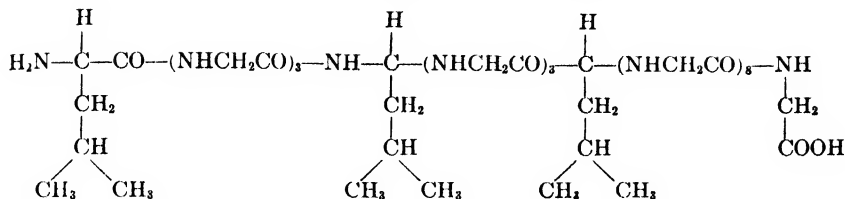
<sup>150</sup> T. Barrati and J. W. Lewis, *Trans. Text. Inst.*, 1922, 13, 113; *J.C.S.*, 1922, 122 (1), 527.

<sup>151</sup> J. R. Katz, "Quellung der Cellulose," in K. Hesse, "Die Chemie der Cellulose und ihrer Begleiter," Adak-Verlagsges.m.b.H., Leipzig, 1928.

<sup>152</sup> L. Balbiano and D. Trasciatti, *Ber.*, 1900, 33, 2323; *J.C.S.*, 1900, 78 (1), 632. L. Balbiano, *Ber.*, 1901, 34, 1501; *J.C.S.*, 1901, 80 (1), 454. See also T. Curtius and F. Goebel, *J. prakt. Chem.*, 1888, (2) 37, 150; *J.C.S.*, 1888, 54, 578.

<sup>153</sup> T. Curtius, *Ber.*, 1904, 37, 1284; *J.C.S.*, 1904, 86 (1), 477. *J. prakt. Chem.*, 1904, (2) 70, 57.

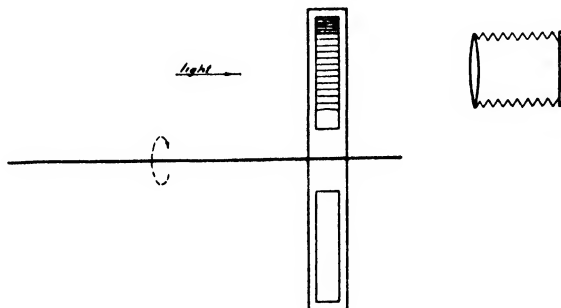
<sup>154</sup> E. Fischer, *Ber.*, 1913, 46, 3078; 1919, 52, 809; 1906, 39, 530.



Svedberg and co-workers<sup>154</sup> have elucidated to a great extent the molecular weights<sup>155</sup> of proteins by measuring sedimentation equilibrium in the ultracentrifuge and also by measuring the sedimentation velocity in a very much stronger cen-

Fig 7.

Principle of Ultracentrifuge.



Courtesy Industrial and Engineering Chemistry  
Courtesy J B Nichols

trifugal field<sup>156</sup> (See Figs. 7, 8 and 9) It was found that proteins formed isodisperse particles, that is, of single molecular weight and that many of the proteins have molecular weights that are multiples of egg albumin.<sup>157</sup> (See Table 7.) By combining the determination of the sedimentation equilibrium and the sedimentation velocity, it is possible to obtain a measure of the deviation of the particle from the spherical shape. By means of these calculations, it was found that protein molecules with molecular weights of 1 or 6 times 34,500 are sensibly spherical whereas those of integrals 2 and 3 are presumably non-spherical.

<sup>154</sup> T. Svedberg and R. Fahrensen, *JACS*, 1926, 48, 430; and J. B. Nichols, *ibid.*, 1923, 45, 2910, and H. Rinde, *ibid.*, 1924, 46, 2677. For reviews on the method see T. Svedberg, "Centrifugal and Diffusion Methods for the Study of Dispersity and Hydration in Sols" in J. Alexander, "Colloid Chemistry," Chemical Catalog Co., Inc., New York, 1926, I, 838. See also T. Svedberg, *Chem. Reviews*, 1934, 14, 1. J. B. Nichols, *Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 12. J. B. Nichols (*Nature*, 1930, 125, 814; *Chem. Abs.*, 1930, 24, 4202) compared the molecular weight determinations by ultracentrifugal measurements with ebullioscopic methods and found them to be sensibly co-ordinated. J. W. McBain, C. R. Dawson and H. A. Barker (*JACS*, 1934, 56, 1021) have studied the diffusion of colloids and colloidal electrolytes and especially egg albumin. From their work it appears as if diffusion through porous membranes was one of the simplest, quickest and most accurate methods of determining particle size or molecular weights. For egg albumin a value of 34,000 was obtained for the molecular weight at the isoelectric point. This compares well with the ultracentrifugal method. Other values of pH brought divergent results apparently due to mutual acceleration and retardation of ions.

<sup>155</sup> There is some question as to whether the determination under these conditions is actually the molecular weight or the weight of the separate particles or micelles.

<sup>156</sup> When a solution is centrifuged in a closed cell for a sufficiently long time, equilibrium results between sedimentation and diffusion. The time required for a quantity of the solute to be driven down by centrifugal force is then the same as that wandering in the direction of rotation through diffusion. To determine the molecular weight it is only necessary to measure the relation between the concentration of the solution at two points from the center of rotation. This value together with temperature, speed of the centrifuge, the partial specific volume of the solute and the density of the solvent allows calculation of the molecular weight.

The velocity of sedimentation may be obtained by using very much stronger centrifugal fields, that is, from 30,000 to above 400,000 times the force of gravity. (A field of 400,000 requires a rotor moving at 75,000 r.p.m.)

<sup>157</sup> W. T. Astbury and H. J. Woods (*Nature*, 1931, 127, 663; *Brit. Chem. Abs. A*, 1932, 752) considered the multiples in the polypeptides to be due to vibrational instability of peptide chains when they became greater than a certain limit.

TABLE 7.—*Molecular Weights of Proteins.*

Protein	Molecular Weight	Ref.*
Egg albumin.	34,500	a
Hemoglobin.	68,100	b
Serum albumin	67,500	c
Serum globulin.	103,600	d
Phycocyan . . .	106,000	e
Phycocerythrin.	208,000	e, f
Edestin .	212,000	g
Lamulus-hemocyanin	2,040,000	h
Helix-hemocyanin	5,000,000	h

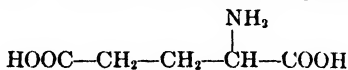
\* T. Svedberg a) and J. B. Nichols, *JACS*, 1926, 48, 3081, b) and R. Fahraeus, *ibid*, 430; c) and B. Sjorgen, *ibid*, 1928, 50, 3318, d) and N. B. Lewis, *ibid*, 525; e) and T. Katsurai, *ibid*, 1929, 51, 3574, f) and A. J. Stamm, *ibid*, 2170, g) and F. F. Heyroth, *ibid*, 539, and h) and E. Chirnoaga, *ibid*, 1928, 50, 1399



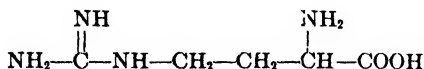
Courtesy Sharples Corp.

FIG. 8.—A Super-centrifuge Used for Separation of Proteins.

Wool, without doubt, is also constructed from long polypeptide chains although much is not known concerning the structure.<sup>158</sup> Two important amino acids which are obtained from wool by hydrolytic cleavage are glutamic acid:



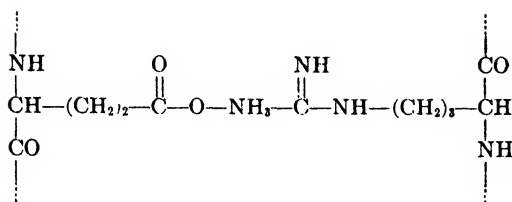
and arginine



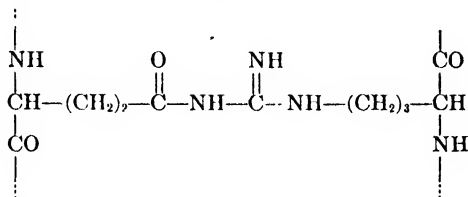
These acids are polyfunctional and may induce cross linkages between the chains of the polypeptides forming a ladder-like structure.<sup>159</sup> This may be accomplished through a salt-like linkage

<sup>158</sup> W. T. Astbury and R. J. Woods, *J. Text. Inst.*, 1932, 23, 127; *Brit. Chem. Abs. A*, 1932, 451. See also W. T. Astbury, "The Fundamentals of Fibre Structure," Oxford University Press, London 1933.

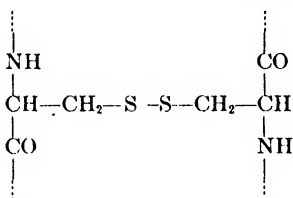
<sup>159</sup> In muscle protein it has been considered that free acidic and basic groups exist in the chains. At the isoelectric point the  $\text{COO}^-$  and  $\text{NH}_3^+$  ions may attract and pull the chain into a spiral. This has been offered as a mechanism for muscular contraction. (See K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," 1930, 238.)



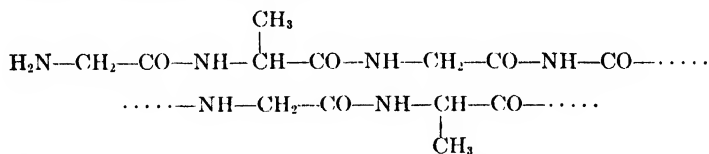
or through a definite polypeptide linkage



Another important amino acid found in the hydrolytic products is cystine. This acid is likewise polyfunctional and can directly bring together two chains:



*Silk* differs from wool in that the amino acids obtained by hydrolytic cleavage contain no sulphur, in other words, cystine is not obtained. The chief amino acids found in silk fibroin<sup>100</sup> are glycine ( $\text{NH}_2\text{-CH}_2\text{-COOH}$ ), alanine ( $\text{CH}_3\text{-CH(NH}_2\text{)-COOH}$ ) and tyrosine ( $p\text{-NH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{CH(NH}_2\text{)-COOH}$ ). The formula for silk fibroin has been considered tentatively as follows:<sup>100a</sup>



Von Weimarn<sup>101</sup> disintegrated natural silk, coagulated and dried the coagulant. Instead of a flexible substance, he obtained a brittle resinous glass-like mass. The method of accomplishing this is as follows. Silk wadding was gradually added to hot aqueous sodium thiocyanate (86-120°C.) and the silk was dispergated under these conditions. After dialysis and subsequent standing the silk solidified to an elastic jelly, which, on further standing, developed syneresis and eventually yielded a perfectly solid glass.

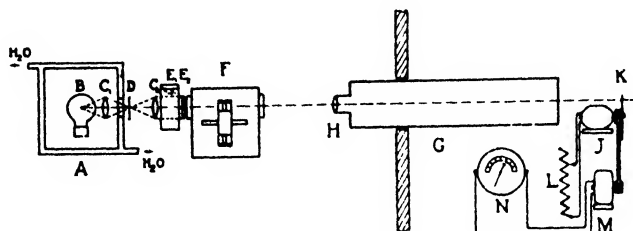
The wet masses, however, could be pulled into threads, especially in the presence of aggregators. Those salts which readily dispergate silk are poor aggregators.

<sup>100</sup> For the studies on the colloidal behaviour of silk sericin, see H. Kaneko, *Bull. Chem. Soc., Japan*, 1934, 9, 207, 241, 283, 409, 344, 461, 510; *Brit. Chem. Abs.* A, 1934, 842; B, 1934, 878; A, 1934, 1069, 1172, 1306; 1935, 33, 165.

<sup>100a</sup> K. H. Meyer and H. Mark, *Ber.*, 1928, 61, 1932.

<sup>101</sup> P. P. von Weimarn, "Dispergation and Aggregation" in J. Alexander, "Colloid Chemistry," IV, 363.

gators. By adding in a thin stream silk solutions in solutions of salt dispergators into concentrated solutions of aggregators, threads of good quality can be produced. When the mass was pulled into threads by one simple pull and dried, a



Courtesy Industrial and Engineering Chemistry  
Courtesy J. B. Nuhols

FIG 9—Optical System for Oil-Turbine Ultracentrifuge

- |                            |  |
|----------------------------|--|
| A, Water-cooled lamp house | H, Objective                           |
| B, Lamp or mercury arc     | J, Motor                               |
| C, Water filter            | K, Stroboscope disk                    |
| D, Light filter            | L, Resistance                          |
| E, Shutter                 | M, Magneto generator                   |
| F, Centrifuge              | N, Hot wire ammeter, readings in r p m |
| G, Camera                  |  |

brittle thread resulted. On stretching and relaxing the thread several times before drying, silk threads were formed which appeared to surpass natural silk

### FIBER STRUCTURE

There is now almost conclusive evidence that materials which form threads and fibers are built up of molecules in which the length is very much greater than any other dimension. The analogy has been drawn to floating logs. Their natural orientation is that pointing down stream and they will travel in that position even if they enter in a random manner. Solutions of many highly polymerized compounds including rubber, cellulose derivatives and polystyrenes exhibit the phenomenon of streaming double refraction.<sup>152</sup> This same phenomenon is observed in sols which on stirring yield marked streaks and in liquids that are just beginning to crystallize and therefore contain very fine crystals.<sup>153</sup> Particles suspended in a streaming liquid have both translatory and rotational motion about their centers of gravity. Elongated particles tend to be oriented; this tendency, however, is opposed by the Brownian movement.<sup>154</sup> Kuhn<sup>155</sup> inferred that the flow double refraction of rubber, gelatin and polystyrene solutions occurs only when a flow gradient is set up. The disperse particles cannot be linear when they are at rest but are coiled up in such a manner that they become effectively isotropic.

Astbury and Woods<sup>156</sup> have deduced from x-ray investigation that fibers may exist in fully extended molecules in such compounds as cellulose, natural silk, stretched wool or hair and stretched rubber. "Folded" or coiled molecules exist in unstretched hair and rubber. X-Ray photographs of stretched hair yielded a diffraction pattern which resembled closely that given by natural silk at all

<sup>152</sup> R. Signer, *Z. physik. Chem.*, 1930, 150, 257; *Brit. Chem. Abs. A*, 1930, 1367.

<sup>153</sup> See H. Freundlich, "Colloid and Capillary Chemistry," trans. H. S. Hatfield, New York, E. P. Dutton and Co., 1922, 408.

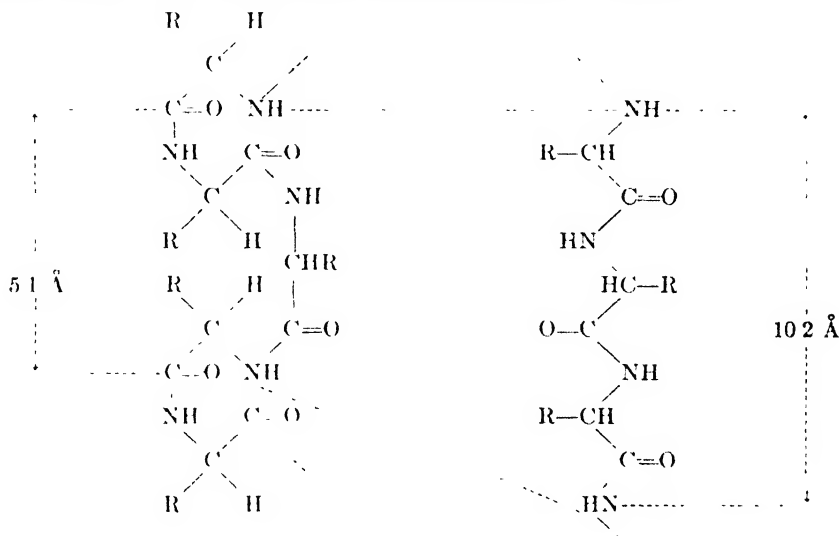
<sup>154</sup> W. Kuhn, *Z. physik. Chem.*, 1932, 161, 1; *Brit. Chem. Abs. A*, 1932, 993.

<sup>155</sup> W. Kuhn, *ibid.*, 1932, 161, 427; *Brit. Chem. Abs. A*, 1932, 1201.

<sup>156</sup> W. T. Astbury and H. J. Woods, *J. Text. Inst.*, 1932, 23, 127; *Brit. Chem. Abs. A*, 1932, 451. See also W. T. Astbury, "Fundamentals of Fibre Structure."

stages of extension. Other proteins which give similar diagrams are collagen in sinews<sup>107</sup> and to some extent in hide and gelatin.<sup>108</sup> Similarly, the photograph of rubber agrees with that which would be expected from polymerized isoprene in the form of chains extended in the direction of stretching. The extended molecules lack elasticity, and fibers built up from such molecules extend through "internal" slippage. Folded molecules can be unfolded allowing the fiber to expand, thus conferring considerable elasticity.

In wool, the change is from the folded keratin molecules (known as  $\alpha$ -keratin) into the longer molecules ( $\beta$ -keratin). The transformation of  $\alpha$ -keratin to  $\beta$ -keratin can be arrested by drying the wool just as it is possible to check the contraction of rubber by cooling. When this stretching process is carried out in boiling water or steam, an extension of something like 100 per cent takes place without rupture; under these conditions there is a complete transformation to the  $\beta$ -form. The skeleton of the unstretched keratin is considered to consist of a polypeptide chain folded into a series of hexagons which are in effect diketopiperazine rings. The rearrangement can be pictured as follows:



Mark<sup>109</sup> has made calculations as to the strength of textile fibers. Assuming that the fiber is made up of infinitely long chains and further assuming that the tensile strength represents the work necessary to break a primary valence bond, he arrives at a figure of 800 kg. per square millimeter for cellulose. This value is much too high. These chains, however, are not infinitely long and moreover the break may occur not through the severance of a primary bond but by the slippage of the chains which are held together by van der Waal's forces. This supposition still assumes that the fibers are in perfect orientation; local imperfections occur which lower this value markedly.

The similarity of silk and cellulose fibers in respect to tensile properties rests

<sup>107</sup> R. O. Herzog and W. Jancke, *Ber.*, 1920, 53, 2162. *Chem. Abs.*, 1921, 15, 131. For X-Ray diffraction studies of surgical catgut ligatures see G. L. Clark, R. H. Flege and P. F. Ziegler, *Ind. Eng. Chem.*, 1934, 26, 440 and P. F. Ziegler and G. L. Clark, *Surgery, Gynecology and Obstetrics*, 1934, 58, 578.

<sup>108</sup> J. R. Katz and O. Gerngross, *Kolloid-Z.*, 1926, 39, 180. *Chem. Abs.*, 1926, 20, 3608. See also O. G. Gerngross and J. R. Katz, *Kolloid-chem. Beihfte*, 1926, 23, 368. *Chem. Abs.*, 1926, 20, 3835.

<sup>109</sup> H. Mark, *Melland. Texturber.*, 1929, 10, 695. See also H. Mark, *Scientia*, 1932, 51, 405, *Chem. Abs.*, 1932, 26, 4467.

on analogous constitution. Assuming the molar cohesion of glyceryl residues to be about 11,600 calories, a chain of 100 peptide units (length 350 Å. U.) would have a molecular cohesion of over  $10^6$  calories. This approaches the value of the cellulose chain.<sup>170</sup>

#### METHODS OF DETERMINING THE MOLECULAR WEIGHT OF POLYMERS

As has already been indicated, ultracentrifugal methods have been used for the determination of the molecular weight of the proteins. In this instance the proteins show uniform particles. Polymerization processes, however, yield a variety of products in the form of polymer homologues and inasmuch as no homogeneous substance is present, the molecular weight represents only an average value. When fractionation of the sample is achieved, there is a much closer approximation to a uniform product and the size of the molecule becomes a matter of considerable interest.

In many instances the size of the molecule and its structure may be partially determined through density, index of refraction, solubility and volatility in comparison with analogous compounds. The method consists in preparing a series of compounds having the same structural unit. From the lower more soluble polymers molecular weights can be obtained and results extrapolated to the higher values.

In the case of molecules of known basal units and known end groups but unknown chain length, it is possible to determine the molecular weight by estimating the end groups quantitatively. Further, knowing that there are two terminal groups in each molecule and with an exact knowledge of the molecular chain, its precise length may be calculated.

The relation between molecular weight and viscosity has yielded interesting results as developed by Staudinger.<sup>171</sup> Earlier experiments in this field were concerned more with low-molecular weight compounds;<sup>172</sup> Staudinger, however, worked with colloids and divided them into two classes on the basis of the viscosity. In one class were those colloids whose molecules were spherical, such as suspensoids and emulsoids. In the second class were included compounds which were non-spherical and were of fiber structure; this second class was further subdivided into association colloids and molecular colloids.

In the low-molecular-weight spherical molecules, the specific viscosity is independent of the molecular weight because this property depends on the number of particles in solution. Under these conditions Einstein's<sup>173</sup> rule is valid in that the viscosity depends wholly on the volume of the disperse phase, in other words, on the concentration. Long molecules behave differently, however. The viscosity

<sup>170</sup> K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe."

<sup>171</sup> For reviews by H. Staudinger, see *Metallborse*, 1930, 20, 1911; *Chem. Abs.*, 1930, 24, 5294; *Ber.*, 1934, 67, 1242; *Brit. Chem. Abs. A*, 1934, 874; *Helv. Chim. Acta*, 1932, 15, 213; *Chem. Abs.*, 1932, 26, 2632; *Ber.*, 1932, 65, 267; *Chem. Abs.*, 1932, 26, 267; *Z. physik. Chem.*, 1931, 153A, 391; *Ber.*, 1928, 61, 2427; *Brit. Chem. Abs. A*, 1929, 51. Application of method to cellulose: H. Staudinger, *Ber.*, 1931, 64, 1688; *Brit. Chem. Abs. A*, 1931, 1040. H. Staudinger and O. Schweitzer, *Ber.*, 1930, 63, 3132; *Brit. Chem. Abs. A*, 1931, 202. H. Staudinger, K. Froy, W. Stark and G. Widmer, *Ber.*, 1930, 63, 2308. For criticism see K. H. Meyer and H. Mark, *Z. Elektrochem.*, 1934, 40, 728; *Chem. Abs.*, 1935, 29, 597. For H. Staudinger's reply cf. *ibid.*, 729; *Chem. Abs.*, 1935, 29, 597. Methyl cellulose: H. Staudinger and H. Scholtz, *Ber.*, 1934, 67, 84; *Chem. Abs.*, 1934, 28, 1589. Acetyl cellulose: H. Staudinger and H. Freudenberg, *Ber.*, 1930, 63, 2331. Polysaccharides: H. Staudinger and O. Schweitzer, *Ber.*, 1930, 63, 2317. H. Staudinger and H. Freudenberg, *Ber.*, 1933, 66, 76; *Brit. Chem. Abs. A*, 1933, 149.

For other discussions, see H. G. Bungenberg de Jong, H. R. Krutv and J. Lens, *Kolloid-Beihfte*, 1932, 36, 429; *Chem. Abs.*, 1933, 27, 458. G. U. Schultz, *Z. physik. Chem.*, 1932, 161, 441; *Chem. Abs.*, 1933, 27, 10. For application to silicic acid solutions, see R. Signer and H. Gross, *Ann.*, 1932, 499, 158; *Chem. Abs.*, 1933, 27, 158. Specific polysaccharides: M. Heidelberger and F. E. Kendall, *J. Biol. Chem.*, 1932, 96, 541; *Chem. Abs.*, 1932, 26, 4309.

<sup>172</sup> For a consideration of this work see E. Hatschek, "The Viscosity of Liquids," G. Bell and Sons, London, 1926, Chapter 7.

<sup>173</sup> A. Einstein, *Ann. Physik*, 1906, (4) 19, 289; *Kolloid-Z.*, 1920, 27, 137.

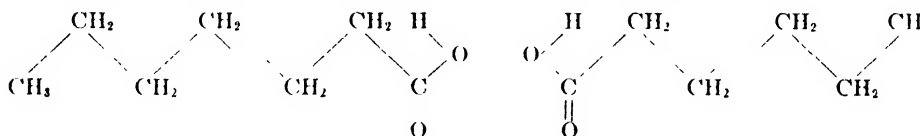


of equally concentrated solutions is not constant but is proportional to the molecular weight. Inasmuch as the molecular weight is proportional to the length of the chain, the viscosity would increase with the length of the molecule and Einstein's rule would no longer hold. Moreover, a difference in the structure of association colloids and molecular colloids may be shown by the alteration of the viscosity of the association colloids on heating due to a disruption of the micellar structure. The long fiber molecules have an elastic structure due to the fact that they exist as a single entity bound by primary valence and on heating the specific viscosity is not altered. The relation between specific viscosity and molecular weight gives an insight into weight and also length of the macropolymers.

The specific viscosity (relative increase in viscosity caused by the solute) of carbon tetrachloride solutions of paraffins, aliphatic esters and ketones is given by the equation

$$\frac{\eta_{sp}}{c} = ny + x$$

where  $c$  = quotient of the concentration in grams per liter by 14, i.e., the molecular weight of the methylene,  $-\text{CH}_2-$ , group  $n$  = number of carbon atoms in the molecule,  $y$  is a constant characteristic of the methylene group and  $x$  a constant which is zero for paraffins but depends on the nature of the groups containing oxygen. For the equation to be valid,  $n$  must be greater than 9. In aliphatic acids it is not the number of carbons in the normal molecule but in the co-ordinated molecule which must be taken into consideration inasmuch as acid particles are present both in solution and in the crystal as co-ordinated double molecules.



In the case of alcohols, however, a lower value is obtained because both the normal (ROH) and the co-ordinated molecules (ROH·HOR) are present. The viscosity determination offers a means of measuring this dissociation. (See Fig. 10.)

Once the constants for the different series were known, a relationship was found between the various hydrocarbon polymers, namely, that equally concentrated solutions are built up of long fiber molecules of the same length whenever the specific viscosity of the solutions is the same. Structure and chemical behavior do not enter into viscosity, only the length of the molecule.

The equation therefore becomes

$$\frac{\eta_{sp}}{c} = Km M$$

where  $c$  is the "grundmolare Konzentration" or the concentration in primary mols.<sup>174</sup>  $M$  is the molecular weight,  $Km$  a constant and  $\eta_{sp}$ , the specific viscosity which is determined from the relative viscosity by the relationship

$$\eta_r - 1 = \eta_{sp}$$

<sup>174</sup> The concentration is expressed in terms of the repeating unit. In the case of polystyrene, the repeating unit is  $-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-$  of molecular weight 104. When  $c = 1$ , there will be 104 g. of the substance in a liter of solution, or  $c = 1$  for a 10.4 per cent solution. The  $km$  constant for the lower fractions of polystyrene polymers was found to be  $1.8 \times 10^{-4}$ . (See Table 8.) Substituting in the equation  $\eta_{sp}/c = Km M$ , the values become  $0.11/0.001 = 1.8 \times 10^{-4} M$ , or  $M = 6.1 \times 10^5$ . For the anomalies which appear in more concentrated solutions of polystyrenes see H. Staudinger and R. Nodsu, *Ber.*, 1930, 63, 717; *Chem. Abs.*, 1930, 24, 717 and H. Staudinger and W. Heuer, *ibid.*, 222; *Chem. Abs.*, 1930, 24, 5716.

The relative viscosity is in turn derived from the relation where the  $t$  (time) is determined from viscosimeter determinations

$$\eta_r = \frac{t \text{ (solution)}}{t \text{ (solvent)}}$$

Ring structures, however, markedly affect the viscosity;<sup>175</sup> thus, solutions of cellulose derivatives are more viscous than solutions of rubber or hydorrubber with

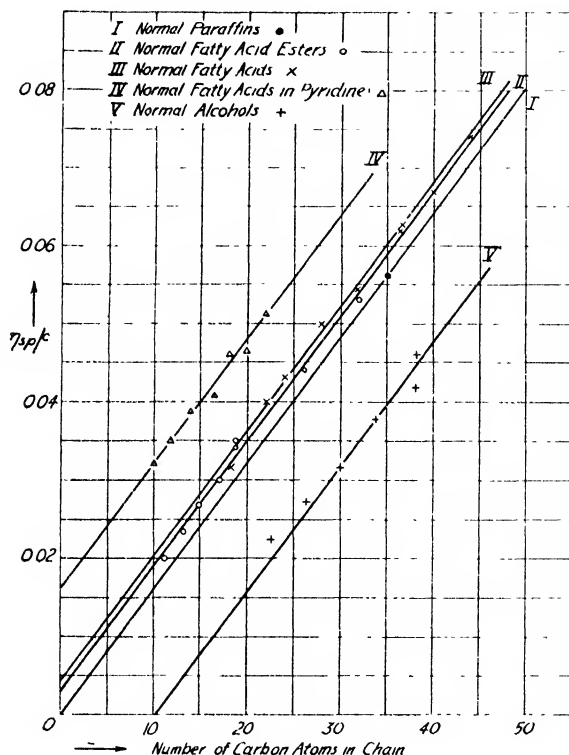


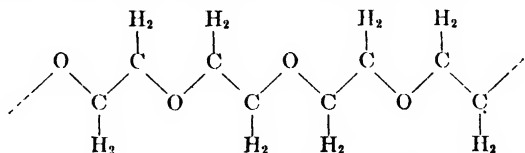
FIG 10

Relation Between Viscosity and Chain-Length of Paraffins and Paraffin Derivatives in 14 per cent Carbon Tetrachloride Solution.

Courtesy H. Staudinger

the same length of molecule because of the presence of the glucose ring<sup>176</sup> (See Table 8.) By preparing analogous compounds having ring members attached to a long and extended chain, the increment in viscosity due to the presence of the ring may be taken into account.

Polyethylene oxide exists in two forms as determined by viscosity measurements.<sup>177</sup> The lower polymers possess the ordinary "zig-zag" configuration.

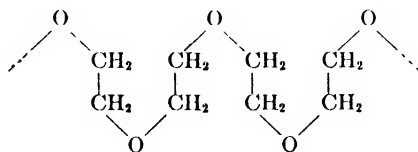


<sup>176</sup> H. Staudinger and E. Ochiai, *Z. physik. Chem.*, 1931, 158, 35; *Brit. Chem. Abs.* A, 1932, 121.

<sup>177</sup> H. Staudinger and R. C. Bauer, *Helv. Chim. Acta*, 1934, 17, 863; *Chem. Abs.*, 1934, 28, 6120.

<sup>177</sup> H. Staudinger, "Die hochmolekularen organischen Verbindungen," 1932, 301 seq.

The higher polymers exist in what is termed the "meandering" form and may be pictured as follows:



The "meandering" form has been substantiated by x-ray determinations<sup>178</sup>

TABLE 8.—Molecular Weight, Specific Viscosity and Chain Length of Highly Polymerized Substances<sup>a</sup>

Compound	$\eta_{sp}$	Conc. in Primary Mols	Content Per Cent	$\eta_p$ $c$	$Km \times$ $10^{-4}$	Aver M W	No. of Atoms Forming Chain	Length in Å
Polystyrene	0 11	0 001	0 01	110 0	1 8	600,000	12,000	15,000
Polyvinyl acetate	0 26	0 0125	0 108	20 8	2 6	80,000	1,800	2,200
Rubber . . .	0 380	0 010	0 068	38 0	3 0	125,000	7,200	8,100
Balata . . .	0 386	0 025	0 17	15 0	3 0	50,000	3,000	3,400
Cellulose . .	0 307	0 0025	0 040	121 4	10 0	120,000	3,800	3,900
Triacetyl cellulose	0 284	0 0025	0 072	113 6	11 0	103,000	1,800	1,900

<sup>a</sup> H. Staudinger, "Hochmolekularen Organischen Verbindungen," p 104

The viscosity values for very high-molecular-weight molecules has been questioned. In the study of the polyoxydecanoic acids,<sup>179</sup> it was found that the molecular weights of the polymers could be obtained by titration up to values of 25,000. These values were checked by ultracentrifuge determinations and were found to be in agreement. Comparison with the viscosity determinations, however, showed that the viscosity method gave reliable values up to a molecular weight of 16,000 but from this point up to a molecular weight of 25,000 increasing errors appear.<sup>180</sup>

Staudinger<sup>181</sup> has replied that the non-agreement really occurs in the lower members of the series as might be anticipated for a highly co-ordinated molecule, whereas much better values are obtained for the range 16,000-25,000. The specific viscosity of a single carbon in the lowest polymer (mol. wt. 780) is  $3.1 \times 10^{-3}$ ; the value falls to  $1.4 \times 10^{-3}$  for a molecular weight of 9300 and remains constant up to the molecular weight of 25,000.

In the relationship

$$\frac{\eta_{sp}}{c} = Km M,$$

the following equation is also valid

$$\frac{\eta_{sp}}{c} = K_1 L$$

where  $L$  stands for the length of the molecule. According to the Einstein law

<sup>178</sup> E. Sauter, *Z. physik. Chem.*, 1933, 21, 161, 186; *Chem. Abs.*, 1933, 27, 3867 Cf. Chapter 50.

<sup>179</sup> W. H. Carothers and F. J. Van Natta, *J. A. C. S.*, 1933, 55, 4714.

<sup>180</sup> E. O. Kraemer and J. Van Natta *J. Phys. Chem.*, 1932, 36, 3175; *Chem. Abs.*, 1933, 27, 1800

<sup>181</sup> H. Staudinger, *Ber.*, 1934, 67, 92; *Chem. Abs.*, 1934, 28, 1589 For other criticisms see K. Hess and B. Rabinowitsch, *Ber.*, 1932, 65, 1856; *Brit. Chem. Abs. A*, 1933, 149. I. Sakurada and S. Lee, *Kolloid-Z.*, 1932, 61, 80; *Chem. Abs.*, 1933, 27, 837. I. Sakurada, *Ber.*, 1934, 67, 1045. R. Obogi and E. Broda (*Kolloid-Z.*, 1934, 69, 172; *Chem. Abs.*, 1935, 29, 1696) compared viscosity and osmotic pressure determinations over a series of concentrations and found that a parallel existed between the viscosity and the molecular weight determinations from osmotic pressure. These investigators consider that Staudinger's relation may be used as an approximate empirical relation up to molecular weights of about 60,000.

the viscosity of the solution is dependent only on the total volume,  $\varphi$ , of the dissolved phase

$$\eta_{sp} = K \varphi$$

For long thin molecules, on the other hand, with the viscosity increasing with the length of the chain, the volume of a chain molecule, effective with respect to viscosity, is not equal to the volume proper but increases with chain length. The effective volume (expressed by Staudinger as a flat cylinder generated by the rotation of a single molecule) can be written as

$$\varphi = \left(\frac{L}{2}\right)^2 \cdot \pi \cdot d$$

where  $d$  is the diameter of the chain. If two chains align themselves to form a single chain, the total effective volume changes from

$$\varphi = N \left(\frac{L}{2}\right)^2 \cdot \pi \cdot d$$

to

$$\varphi = \frac{N}{2} \left(\frac{L}{2}\right)^2 \cdot \pi \cdot d$$

If, on the other hand, the number of chain molecules is halved due to the formation of chains twice the length of one chain, the effective volume changes from

$$\varphi = \frac{N}{2} \left(\frac{2L}{2}\right)^2 \cdot \pi \cdot d$$

to

$$\varphi = 2N \left(\frac{L}{2}\right)^2 \cdot \pi \cdot d$$

The effective volumes, therefore, of chain molecules of different length increase proportionately to the *square* of the length of the chain, that is, to the *square* of the molecular weight.

Because of the large effective volume of the long chain molecules, even their dilute solutions are not ordinary. As the concentration increases, the total effective volume quickly outstrips the available volume. A gel solution can therefore be considered as one where the effective volume of the long molecules is greater than the actual volume of the solution. Such a gel condition can not be obtained with substances of low molecular weight inasmuch as the molecules extend equally in all dimensions, consequently the sphere of activity of a molecule is almost identical with its own volume.

#### THE APPLICATION OF X-RAY METHODS TO MACROPOLYMERS

Mention has already been made concerning the use of x-rays in the elucidation of the structure of certain natural products, the linear polymers. The field of amorphous products is one of the most recent to which x-ray analysis has been applied.<sup>122</sup> Much pioneer work, however, needs to be done although enough has

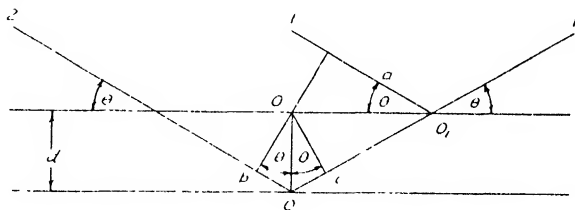
<sup>122</sup> In addition to the references already cited, the following summaries have appeared: G. L. Clark, "Applied X-Rays," McGraw-Hill Book Co., Inc., New York, *Ind. Eng. Chem.*, 1929, 23, 128. S. E. Sheppard, *Ind. Eng. Chem.*, 1931, 25, 781. See also G. Natta, *Giorn. chim. ind. applicata*, 1934, 16, 285; *Chem. Abs.*, 1935, 29, 130. H. Staudinger, "Hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932. R. Houwink, "Physikalische Eigenschaften und Feinbau Natur- und Kunstharzen," Akad. Verlagsges. m. b. H., Leipzig, 1934. K. H. Meyer and H. Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akad. Verlagsges. m. b. H., Leipzig, 1930. For other discussions on x-rays cf. E. Schmid and W. Boas, "Kristallplastizität," J. Springer, Berlin, 1935. A. H. Compton and S. K. Allison, "X-Rays in Theory and Experiment," D. Van Nostrand Co., Inc., New York, 1935.

been accomplished to indicate that x-ray analysis should prove to be a most useful tool.

The first application of x-ray methods was to that of crystal structure. Acting on the suggestion of Laue,<sup>183</sup> Friedrich and Knipping<sup>184</sup> found that a crystal acted as a 3-dimensional optical grating for x-rays. Shortly afterwards the Braggs<sup>185</sup> modified the Laue method to make possible not only the direct determination of the actual arrangement in the crystal but also provide a means of determining the wave length of x-rays.

In the Laue method the rays are passed through the crystal and the image registered on the photographic plate. The image produced is one of a symmetrically arranged group of spots. If, while the photograph is being taken, the crystal is rotated perpendicular to the x-ray beam, all of the spots become arranged on a series of curves, one parallel and the other perpendicular to the axis of rotation.

Fig. 11  
Derivation of Bragg's Law



The Braggs were able to show that the diffraction by the crystal could be treated more easily as reflections from the successive planes of ions (or atoms) rather than a 3-dimensional grating. The treatment is analogous to the refraction of visible light from a stack of very thin plates of glass. The problem is very much simplified, however, if the reflected beam is considered as equal to the angle of incidence (See Fig. 11). Under these conditions, an expression can be developed

$$n\lambda = 2d \sin \theta$$

where  $\lambda$  is the wave length of the light,  $d$  is the distance between the planes,  $\theta$  is the angle of refraction (or the "glancing angle of reflection") and  $n$  is an integer, usually small, called the order of diffraction.

Inasmuch as the crystal has several "faces" or planes (see Fig. 12), the analysis of the crystal structure by the Bragg method involves the determination of the relative spacing of the planes perpendicular to the principal directions of the crystal. Either the naturally occurring planes in the crystal may be used or the planes may be ground on the crystal, either procedure, however, involving the use of a fairly large well-developed crystal. The discovery by Hull<sup>186</sup> and by Debye and Scherrer<sup>187</sup> that the minute crystals present in a crystalline powder could reflect x-rays, opened new fields for x-ray research. It will be noted that under these conditions (see Fig. 13) the photograph is characterized by a series of rings. A crystal rotating about a fixed axis gives rise to a set of single spots. When the crystal is in the powdered condition, each spot will be repeated many times with the resultant effect that rings are produced.

<sup>183</sup> M. Laue, *Sitzb. kais. Akad. Wiss., München*, 1912, 263, *Chem. Abs.*, 1913, 7, 2010 *Ann. Physik.*, 41, 971; *Chem. Abs.*, 1914, 8, 11.

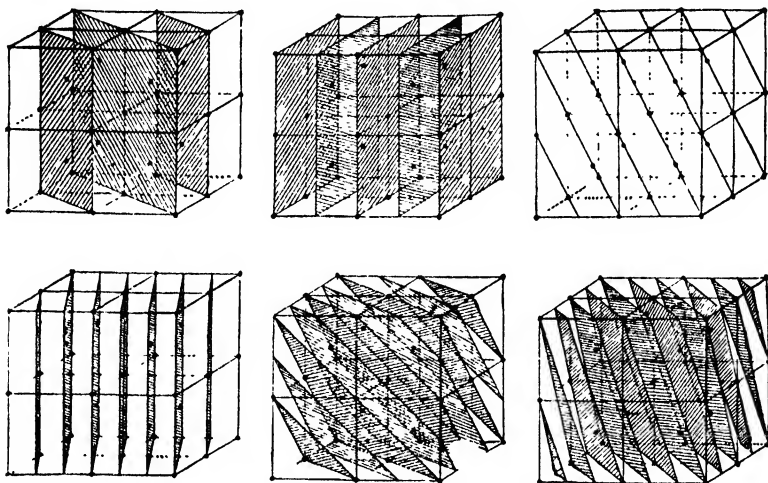
<sup>184</sup> W. Friedrich, P. Knipping and M. Laue, *Sitzb. kais. Akad. Wiss., München*, 1912, 303, *Chem. Abs.*, 1913, 7, 2009 *Ann. Physik.*, 41, 989, *Chem. Abs.*, 1914, 8, 11.

<sup>185</sup> W. H. and W. L. Bragg, "X-Rays and Crystal Structure," 1915. See W. H. Bragg, *J.C.S.*, 1916, 109, 260.

<sup>186</sup> A. W. Hull, *Phys. Rev.*, 1917, 10, 661; *Chem. Abs.*, 1918, 12, 649.

<sup>187</sup> P. Debye and P. Scherrer, *Physik. Z.*, 1916, 17, 277; 1917, 18, 291; *Chem. Abs.*, 1917, 11, 1786; 1918, 12, 786.

No discussion of crystallographic work will be given here,<sup>188</sup> save for the crystal structure of diamond and graphite. (See Fig. 14.) The staggered carbon layers in diamond account for its extreme hardness, while the flat layers of graphite can



*Courtesy G. L. Clark*

FIG 12—Typical Sets of Parallel Planes in a Cubic Lattice.

easily be used to explain the latter's fine lubricating properties, since the bonds from carbon layer to carbon layer may be ruptured easily. Many such examples

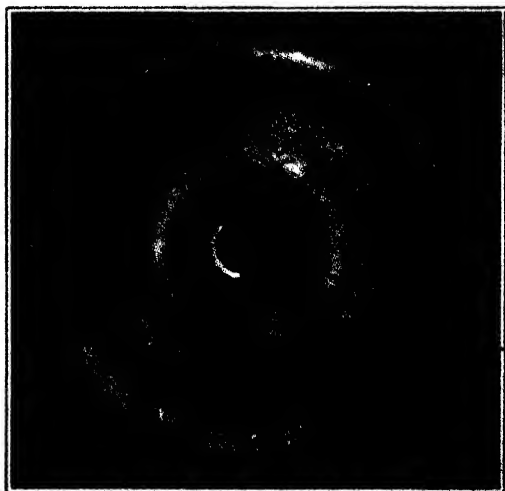


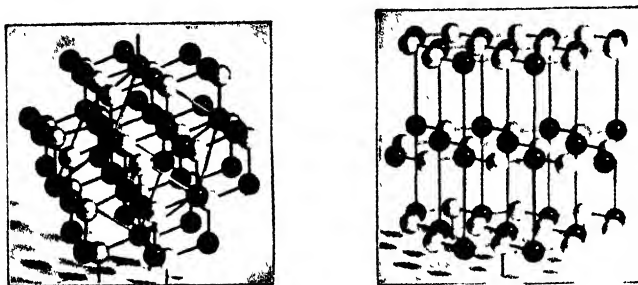
FIG 13.  
A Typical Crystalline Powder  
X-Ray Diagram.

*Courtesy S. E. Shppard*

of the correlation of physical properties and crystal structure are known and undoubtedly the microscopic properties of a solid are influenced to an enormous extent by the properties of the fundamental crystallographic unit.

<sup>188</sup> For further details, bibliography and discussion, see R. W. G. Wyckoff, *J. Franklin Inst.*, 1923, 195, 183, 349, 531 and "The Structure of Crystals," Chem. Catalog Co., N. Y., 1924.

In the study of liquids and amorphous solids such as glasses, resins, colloids and various natural and synthetic organic compounds, the angles of diffraction are not sharp and well defined as in the truly crystalline substances but are quite broad. The x-ray patterns show halos instead of sharp rings or spots. A perfectly amorphous substance should yield a diffraction pattern consisting essentially



*Courtesy Central Scientific Co*

FIG. 14—The Structures of Diamond and Graphite as Deduced by X-Ray Diffraction Methods

of only a general fogging with no signs of halos or preferred scattering at any angle. Any kind of an arrangement of the ultimate units in an imperfectly amorphous material, of the most rudimentary variety, would result in the registration of a broad halo upon the photographic plate. A single broad diffraction halo indicates, at least, an elementary tendency toward organization. Liquids



FIG. 15.  
A Typical X-Ray Diffraction Pattern of a Liquid

*Courtesy S. E. Sheppard*

(see Fig. 15) and gases are known to produce such halos so that even here we are not dealing with perfectly amorphous substances. It seems likely that these halos, simple as they are, measure some fundamental periodicity associated with the pseudo-amorphous solid.

A measurement of the diameter of the halo together with its breadth and intensity with respect to the general background yields information which, when

properly interpreted, is of considerable significance. Especially is this true, in the case where it is desired to show that two substances, although of identical chemical composition and prepared by similar methods, are fundamentally different. This difference may arise in a slight shift in the halo, a change in its breadth or an alteration of the intensity. If the substances are different, perfectly matched x-ray patterns do not occur.

It can be seen, therefore, that although the theoretical nature of the origin of the halos of these pseudo-amorphous substances is at best imperfectly understood, information can still be obtained. When this information is properly correlated with physical and chemical data, conclusions of considerable significance may be expected.

**Experimental Procedure.** In Figure 16 is a diagrammatic sketch of the general experimental set-up. The figure shows a Muller-Femstruktur copper x-ray tube hav-

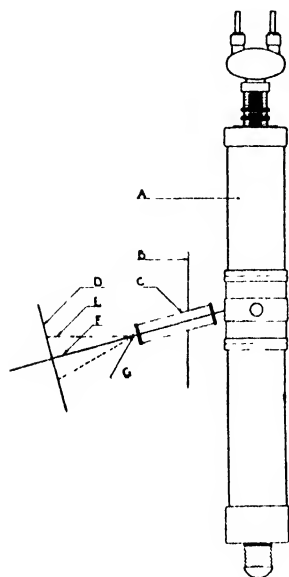


FIG. 16

A Muller Femstruktur X-Ray Tube (See Fig. 17)

A. X-Ray Tube

B. Lead Shield

C. Lead Pinholes

D. Photographic Plate

E. Diffracted Ray

F. Central Undeviated Ray

G. Specimen

Courtesy G. L. Clark

ing an operating voltage of about 30,000 volts and 25 milliamperes. The x-ray beam of 1.54 Ångstrom units ( $1.54 \times 10^{-8}$  cm.) wave length is defined by two .025-inch lead pinholes. The distance from the plate to the specimen under examination is 300 cm. Samples are usually adjusted to 1 mm. thickness. The mounting is fixed and the beam of x-rays transmitted perpendicularly. In general, to obtain accurate results care is taken with the time of exposure of films, control of voltage and amperage of the x-ray tube and finally with the development of the negative. The developed negatives are best compared by obtaining intensity curves which allow breadth of the rings, the intensity and the distance from the source to be read directly.

Beal, Anderson and Long<sup>109</sup> studied the resins obtained from the polymerization of cumarone and indene<sup>100</sup> by x-ray methods. (See Figs. 18 and 19) The resins made by polymerizing a coal tar naphtha distillate were not amorphous but gave well-defined rings which indicated fundamental spacings within the resin molecules. (See Table 9.)

<sup>109</sup> F. Beal, H. V. Anderson and J. S. Long, *Ind. Eng. Chem.*, 1932, 24, 1068

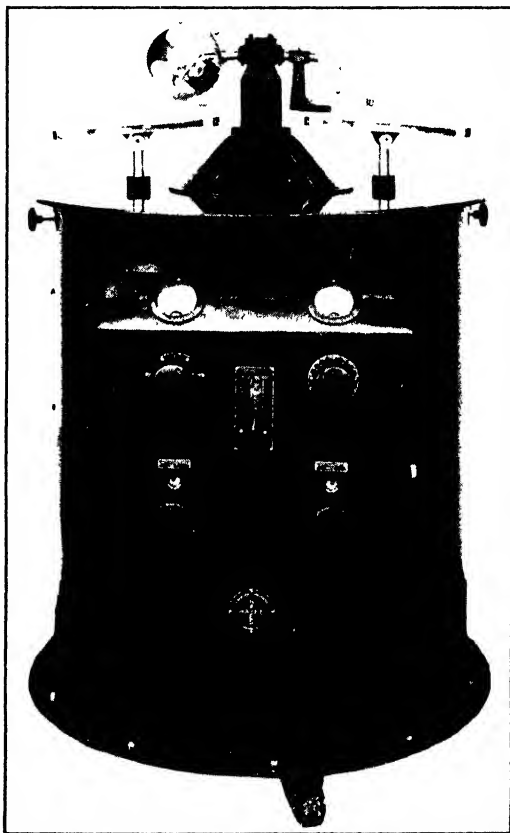
<sup>100</sup> See Chapters 5, 6 and 7.



TABLE 9.—*Cumarone-Indene Resins*

	Melting Point m °C.	Ångstrom Units		
		$d^1$	$d^2$	$d^3$
Crude naphtha	—	—	5 3	—
Liquid resin	—	2 3	7 5	9 4
Soft resin	20	2 2	5 3	9 2
Medium soft resin	80	2 3	5 3	9 4
Hard resin	132	2 2	5 2	9.3
Nevindene	153	2 2	5 2	9 4
Nevindene	178	—	5 3	9 1

Little could be learned concerning the effects of polymerization, except that: "Any theory for explaining the polymerization of the resin must take into account



*Courtesy Prof. G. L. Clark*

FIG. 17.—X-ray Diffraction Equipment at the University of Illinois.

several factors revealed by x-ray data. (1) The 5.3 Å spacing is evidently caused by the thickness of the individual cumarone and indene molecules, and since this spacing persists in the highly polymerized resin, the molecules must be so combined that their thickness can still give rise to an intensity maximum. (2) In the polymerization process, a new arrangement of the molecules giving rise to a spacing of 9.1 Å is formed; and (3) in the liquid resin, which is a very low polymer, the

spacing due to the thickness of the molecule has disappeared." They further suggested that the molecules first polymerize into groups which possess the thickness of the single molecule. The thickness spacing is lost at this stage due to random arrangement. As polymerization proceeds, the molecules align themselves into layers separated by a distance equal to the thickness of the individual

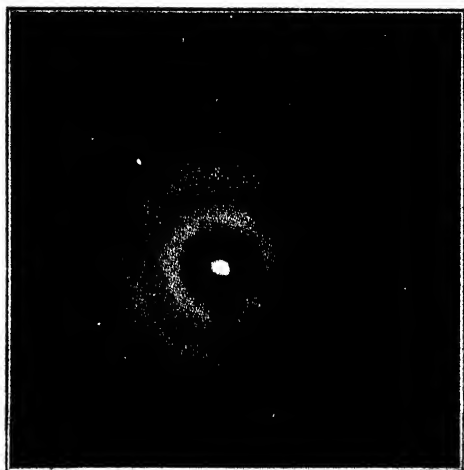


FIG. 18.  
Indene, Copper Radiation.

*Courtesy F. Beal, H. V. Anderson and J. S. Long*

molecule, thus bringing about the reappearance of the 5.3 Å spacing. That it returns unchanged is taken as evidence that the layering is due to forces other than primary chemical valencies. The precise origin of the outer spacing is not

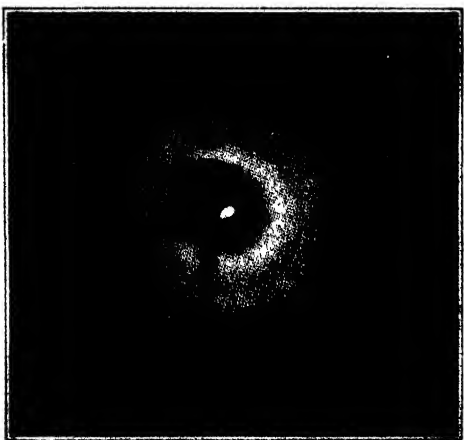


FIG. 19.  
Indene, Copper Radiation

*Courtesy F. Beal, H. V. Anderson and J. S. Long*

clear, but the 2.2 Å ring is found to appear in many natural resins. Possibly the reappearance of the 5.3 Å ring is due to the production in the later stages of polymerization of a new repeating unit, not identical with that giving rise to the first 5.3 Å spacing.

Trillat<sup>191</sup> and others, including the author,<sup>192</sup> have investigated the condensation products of phenols with formaldehyde with respect to the x-ray patterns. In Table 10 are given the results which are very interesting when analyzed in the light of polymerization phenomena, fusibility and solubility and bear out the current theories concerning the structure of the phenol-formaldehyde type resin.<sup>193</sup>

TABLE 10.—*Phenol-Formaldehyde Resins*

Resin	$d^1$	$d^2$	$d^3$	Ref. or Fig
Phenol-formaldehyde. . . . .	3 5 Å	4 6 Å	—	(*)
o-Cresol-formaldehyde . . . . .	3 5 Å	5 0 Å	—	(*)
m-Cresol-formaldehyde. . . . .	3 6 Å	5 0 Å	—	(*)
p-Cresol-formaldehyde. . . . .	3 5 Å	4 6 Å	—	(*)
Xylenol-formaldehyde (liquid) . . . . .	4 1 Å	5 5 Å	17 5 Å	20 <sup>b</sup>
Xylenol-formaldehyde (soft). . . . .	4 2 Å	5 5 Å	14 7 Å	21
Xylenol-formaldehyde (infusible) . . . . .	4 2 Å	5 9 Å	15 4 Å	22
Xylenol-formaldehyde (fusible) . . . . .	4 2 Å	6 2 Å	12 65 Å	23

<sup>a</sup> Data from R. Houwink, "Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen."

<sup>b</sup> The numbers refer to illustrations

In the study of synthetic resins and compounds of the type which are susceptible to polymerization, the determination of the intensity of the lines is of the utmost importance. From the above table it will be seen that in proceeding from the phenol to the xylenol resin, the tendency is to form larger spacings. This tendency, especially for the spacings labeled  $d^1$  and  $d^2$ , is probably increased by the side chains on the aromatic nucleus. Thus one would expect to find that a greater increase in  $d^1$  and possibly  $d^2$  will be found in an o-butylphenol-formaldehyde resin, less of the same tendency in a p-butylphenol resin. In resins 20, 21 and 22 it will be seen that as polymerization proceeds the intensity of the rings becomes less and less. An examination of the intensity curves for these resins reveals that the curves are becoming less undulating, that is, the difference between trough and crest is becoming less and less. The lessening of intensity of the outer halo shows greater spatial distances, indicating a greater degree of polymerization. The resin marked 23 is a fusible xylenol resin; its x-ray properties approximate that of the potentially reactive soft resin 21.

In Table 11 and Figures 24, 25 and 26 are given three different stages of the same phenol-formaldehyde resin: 24 is the phenol-formaldehyde resin made by refluxing 1 mol phenol with 1.5 mols of formaldehyde in the presence of sodium carbonate, and dried *in vacuo*; 25 is the same resin cured under 3000 pounds per square inch at 120-130°C.; while 26 is the same resin compressed at 3000 pounds per square inch at 70°C., then removed from the press and heated in an oven at 70°C. with the temperature gradually rising to 140°C. until cured.

TABLE 11.—*Phenol-Formaldehyde Resin in Various Stages of Polymerization*

Resin	$d^1$	$I^1$
24). . . . .	4 8 Å	3
25).... .	5 2 Å	24
26)..... .	5.3 Å	33

In this case only one ring can be detected. The intensity curves are smooth and broad, broadening as heating is continued, indicating an increased degree of

<sup>191</sup> J. J. Trillat, a. "Reservement des Groupements." b. "Les applications des rayons-X," Paris, 1930.

<sup>192</sup> Carleton Ellis, private communication from Ellis-Foster Company.

<sup>193</sup> Acknowledgment is made to Dr. G. L. Clark of the University of Illinois for his help in this work.

polymerization. The maximum shifts to a somewhat larger value as polymerization increases, as does the intensity. In the primary resin the single band is well defined and narrow but polymerization causes a broadening and a smoothing which indicates random clustering of primary aggregates with less approach to orientation.

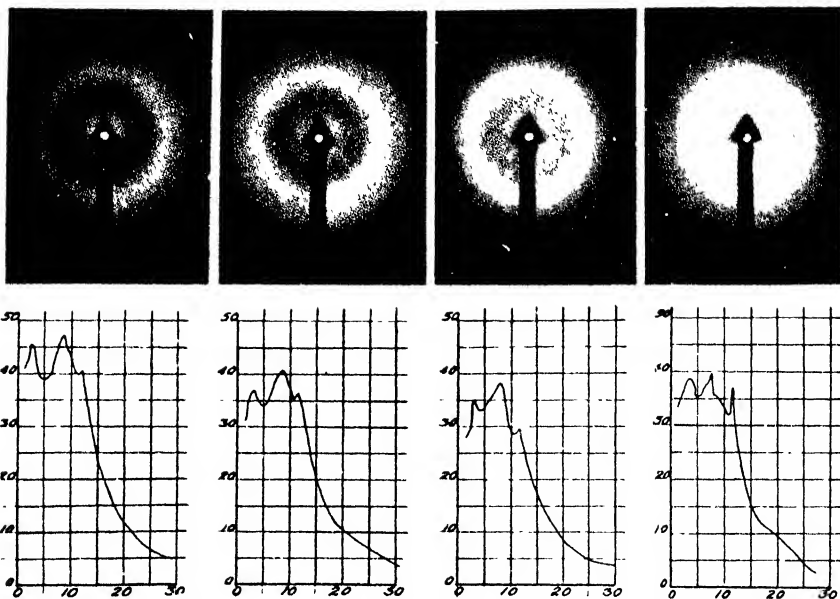


FIG 20

FIG 21

FIG 22

FIG 23

FIGS 20-23.—X-Ray Patterns and Intensity Curves of Various Xylenol-Formaldehyde Resins.

FIG. 20.—A liquid resin made by refluxing 1 mol of mixed xylenols with 15 mols of aqueous formaldehyde in the presence of an alkaline catalyst. Reaction was continued until the xylene-formaldehyde condensate just precipitated. After being washed and then dehydrated at 105°C., the product was a viscous liquid at room temperature. The ordinate of the intensity curve represents percentage darkening of the pattern; the abscissa is plotted in number of millimeters (measured on original negative) from central spot. For conversion curve, see Fig. 27.

FIG. 21.—Soft resin, soluble in toluene and a mixture of toluene and methyl alcohol, prepared by heating liquid xylene-formaldehyde resin at 130-140°C. until a slightly soft product is obtained.

FIG. 22.—An infusible resin soluble in toluene and toluene-methanol mixtures. Softens slightly when heated but is not fusible. It is obtained by heating soft xylene resin until gelation takes place.

FIG. 23.—Fusible resin resulting from the reaction of 1 mol of mixed xylenols and 1 mol of aqueous formaldehyde without an added catalyst.

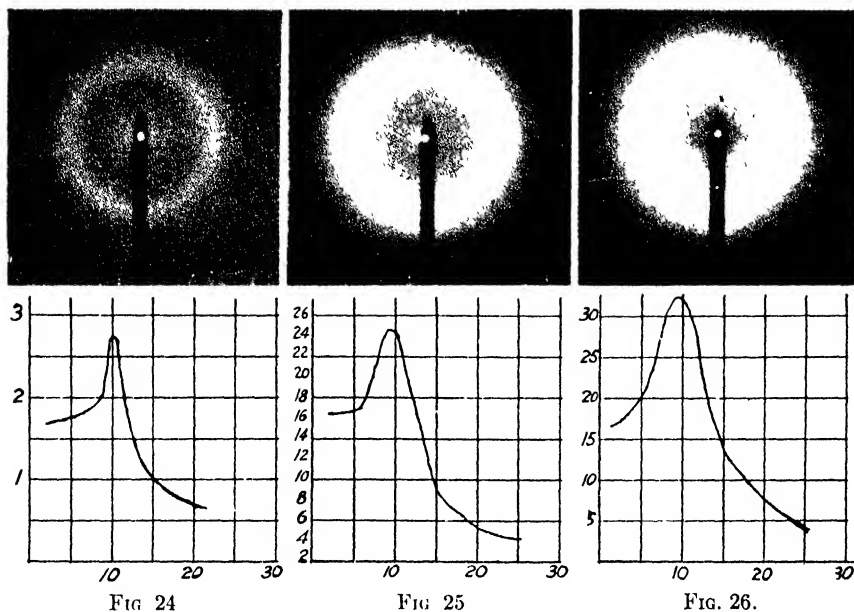
Fatty oil acid modified glycerol phthalate resins<sup>104</sup> offer interesting x-ray patterns. (See Table 12.)

TABLE 12.—Modified Glycerol Phthalate Resins

Resin	$d^1$	$d^2$	$I^1$	$I^2$
28) Stearic glycerol phthalate	4.55	9.32	45	32
29) Linoleic glycerol phthalate	4.60	—	48	—
30) Linoleic-elaeostearic glycerol phthalate.	4.77	2.32	52	39

<sup>104</sup> See Chapter 41 and seq.

Approximately the same degree of fogging near the central spot is taken as a measure of the same degree of polymerization. From the stearic to the linoleic-



FIGS. 24-26—X-Ray Patterns and Intensity Curves of Phenol-Formaldehyde Resins  
 Fig. 24—A potentially reactive resin prepared in the presence of sodium carbonate  
 Fig. 25—Partially cured resin made by heating potentially reactive resin at 120-130°C under 3000 pounds pressure.  
 Fig. 26.—Cured resin made by compressing at 70°C. and 3000 pounds pressure. The resin was removed from press, heated in an oven at 70°C. and then gradually heated to 140°C.

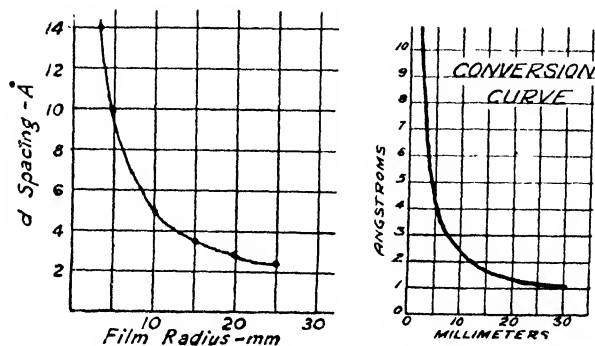


FIG. 27—Conversion Curves for Intensity Graphs, Making Possible the Conversion of Millimeters to Ångstrom Units (see Fig. 20). Graph on left applies to Figs. 24, 25 and 26; the one on the right can be used with all the other intensity curves.

elaestearic phthalic glyceride, however, there is a general smoothing out of the intensity curves signifying an approximation of the truly amorphous state in which the primary aggregates are joined in perfectly random distribution.

In Table 13 and Figures 31, 32 and 33 are data and photographs of glycerol phthalate in different stages of polymerization:<sup>106</sup> 31 is the half-acid ester, 32 is a soft resin and 33 is the hard, infusible, insoluble C-stage.

TABLE 13.—Unmodified Glycerol Phthalate Resins

Resin	$d^1$	$d^2$	$d^3$	$d^4$	$I^1$	$I^2$	$I^3$	$I^4$
31) Half-acid Ester . . .	4 05	4 80	6 30	14 00	40	40 5	36	28 5
32) Soft resin ,		4 55	6 30			33 5	30 5	
33) Infusible and Insoluble		4 55	6 45			39	34 5	

From the patterns it may be seen that in the infusible and insoluble form of the resin there is a great deal of fogging close to the center spot, showing a great

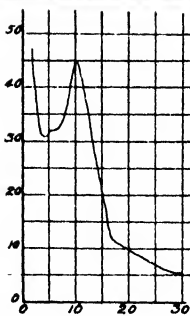
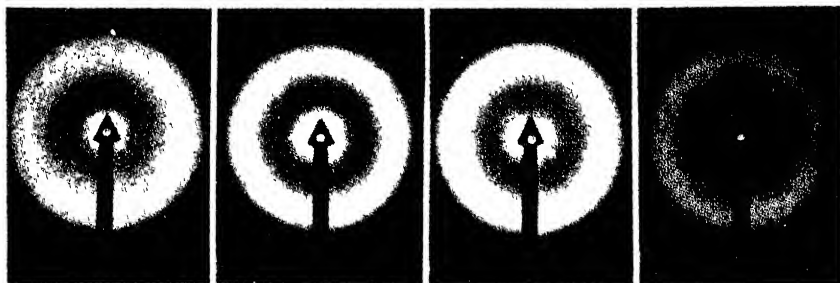


FIG. 28.

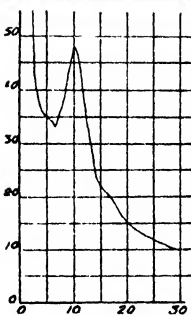


FIG. 29.

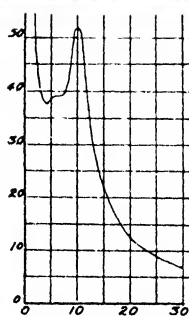


FIG. 30.

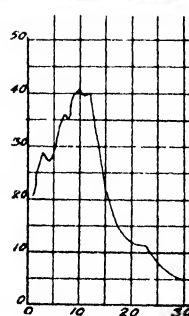


FIG. 31.

FIGS. 28-31.—X-Ray Patterns and Intensity Curves of Glycerol-Phthalic Anhydride Resins.

FIG. 28.—Resin modified with stearic acid.

FIG. 29.—Resin modified with linoleic acid.

FIG. 30.—Resin modified with linoleic and elaeostearic acids

FIG. 31.—Unmodified resin in half-ester stage obtained by heating glycerol and phthalic anhydride to 170°C. The product is a viscous liquid at room temperature.

tendency toward the 3-dimensional polymer. Moreover, the maximum near 8 mm. from the central spot becomes more pronounced as the reaction becomes more complete. This increase in definition of the maximum is explained by an increased tendency for definite orientation and a closer approach to crystallinity. This does not mean crystallinity in the ordinary sense of the word, but an alignment of the molecules of the resin to give the semblance of crystallinity. In other words, the fully cured resin assumes the properties of a macro-pseudo-crystallite.

<sup>106</sup> See Chapter 42.

In casting resins one would expect to observe a similar phenomenon. In this instance, as the resin slowly hardens, orientation to a crystallite state can take place more easily.

A difference may be pointed out between the methods of polymerization of phenolic resins and that of the phthalic glycerides. In phenolic resin the contrast between the maximum and minimum becomes less distinct and the intensity curves have a tendency to become smooth; in phthalic glyceride, however, these curves become more jagged. Polymerization, therefore, is taking place with orientation

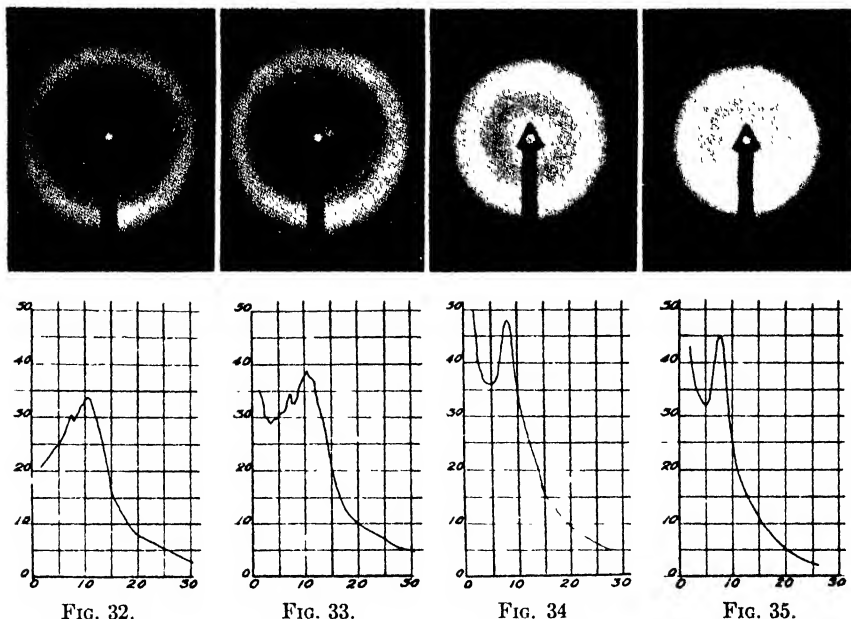


FIG. 32.

FIG. 33.

FIG. 34

FIG. 35.

FIGS. 32-35.—X-Ray Patterns and Intensity Curves of Various Resins

FIG. 32—Soft unmodified glycerol phthalate resin, soluble in methanol, formed by heating glycerol phthalate resin in half-ester stage to 210-220°C. until a brittle product remained. Acid number is 90.

FIG. 33—An unmodified glycerol phthalate resin in the infusible and insoluble stage. This was obtained by heating soft glycerol phthalate resin to 245°C. until gelation took place.

FIG. 34—Rosin-modified glycerol phthalate.

FIG. 35.—Rosin-maleic anhydride adduct.

and hence a nearer approach to the crystalline state. The polymerization of the phenolic resin, on the other hand, takes place through a clustering of primary aggregates with no approach but rather a recession from a crystalline state.

The influence of rosin in the resin molecule may be seen in Figures 34 and 35. The first is a rosin modified phthalic glyceride while the second is a maleic anhydride adduct of rosin.<sup>196</sup> One might say the two substances were identical, so closely do their patterns match. There are some slight differences, only enough to show there are two different substances being examined. Beal, Anderson and Long<sup>197</sup> have studied the products obtained by modifying phenolic resins and phthalic glyceride with ester gum. (See Table 14.)

<sup>196</sup> See Chapter 40.

<sup>197</sup> F. Beal, H. V. Anderson and J. S. Long, *loc. cit.*

TABLE 14.—*Resins Derived from Rosins*

Resin	$d^1$	$d^2$
Wood rosin W. G	2 31	5 75
Ester gum, light .	2 25	5 63
Ester gum, dark	2 25	5 51
Amberol BS/1	2 25	5 57
Amberol 105/F	2 25	5 54
Amberol F-7 .	2 25	5 51
Teglac 6	2 16	5 54
Teglac 15	2 24	5 43
B-K gum	2 16	5 25

Both of these modified resins show precisely the rings associated with raw rosin Esterification with glycerol to form ester gum, as well as the subsequent incor-

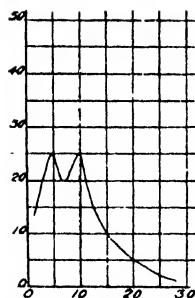
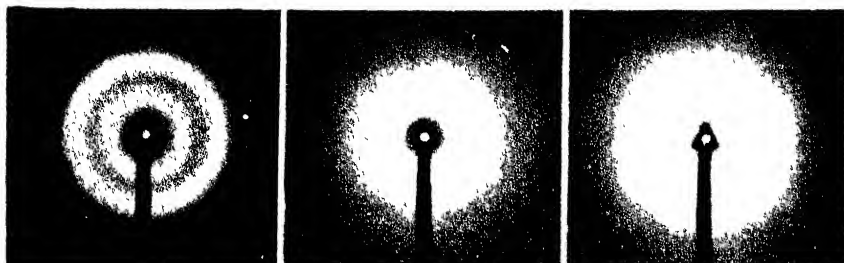


FIG. 36

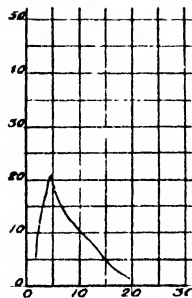


FIG. 37.

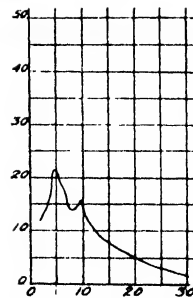


FIG. 38

FIGS. 36-38—X-Ray Patterns and Intensity Curves of Sulphur Resins

FIG. 36.—A glycerol-polysulphide plastic prepared by reacting glycerol dichlorohydrin and sodium polysulphide.

FIG. 37.—An ethylene polysulphide plastic made from ethylene dichloride and sodium polysulphide.

FIG. 38.—A phenol-sulphur chloride resin made by treating 100 g. of phenol with 150 g. of sulphur monochloride.

poration of synthetic materials, has apparently little effect upon the fundamental molecule present in rosin. The fact that even by modifying rosin to such an extent as reacting it with maleic anhydride does not change its character is especially significant. X-Ray methods would seem to offer a positive method of identifying this natural substance in all of its forms in commerce.

Large atoms, naturally having more mass, give more intense lines in the x-ray diffraction patterns and superficially may be detected more easily. In the following series sulphur is the large atom. Such large atoms are predominant throughout a series. In the following table and Figures 36, 37 and 38, 36 is the

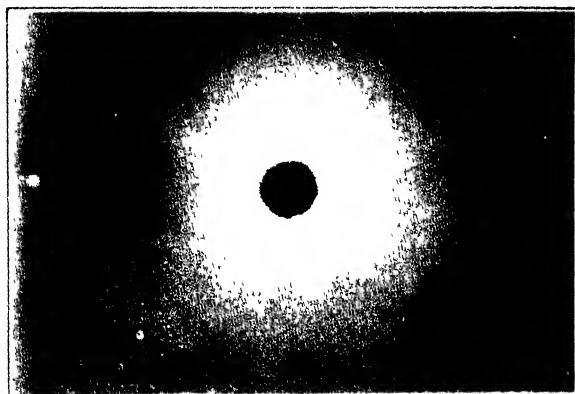


reaction product of glycerol dichlorhydrin-sodium polysulphide; 37 of ethylene dichloride-sodium polysulphide;<sup>196</sup> and 38 of phenol-sulphur chloride.<sup>196</sup>

TABLE 15.—*Sulphur Resins*

Resin	$d^1$	$d^2$	$I^1$	$I^2$
36) Glycerol-Sulphur Resin	4 8	9.32	25	25
37) Ethylene-Sulphur Resin		9 35		21
38) Phenol-Sulphur Chloride Resin	4 8	9 32	16	22

These three substances resemble each other closely as regards their x-ray patterns. Proceeding from glycerol-sulphur to phenol-sulphur and to ethylene-sulphur resin, it is apparent from the intensity curves that the spacing  $d^1$  becomes weaker and weaker until it is finally non-existent. The phenomenon may be due to a greater polymerization existing in the substance, but the explanation is doubtful. No concept at present can be offered for this interesting fact.

FIG 39—X-Ray Pattern of Unstretched Chloroprene.<sup>a</sup>

<sup>a</sup> Courtesy W. H. Carothers. Photograph taken by A. W. Kenney

The behavior of rubber both in the stretched and unstretched states has already been considered. According to Mark<sup>200</sup> all of the synthetic polymerized products from isoprene and other unsaturated hydrocarbons yield, even when stretched, a diffraction pattern analogous to that of a liquid. Duprene or polymerized chloroprene<sup>201</sup> is the first synthetic rubber-like material to give a characteristic x-ray pattern on stretching.<sup>202</sup> (See Figs. 39, 40 and 41.)

Carothers and Hill<sup>203</sup> have made a study of artificial fibers produced from hexadecamethylene dicarboxylic acid and trimethylene glycol. Filaments are produced from the molten ester by touching it with a stirring rod and then drawing the rod away, or by extruding a chloroform solution. If sufficient tension is applied during the spinning, lustrous threads of improved mechanical properties result; otherwise the thread is opaque and lacks luster. The opaque thread shows an x-ray diagram with several fairly well defined rings; with the lustrous material a series of spots is observed, which, while not so complex as in the case of ramie, is of the

<sup>196</sup> See Chapter 58

<sup>199</sup> See Chapter 59

<sup>200</sup> H. Mark, "Die Röntgentechnik in der Materialprüfung," Eggert and Schiebold, Akademische Verlagsges.m.b.H., Leipzig, 1930, 142

<sup>201</sup> See Chapter 8.

<sup>202</sup> W. H. Carothers, I. Williams, A. M. Collins and J. E. Kirby, *J.A.C.S.*, 1931, 53, 4203.

<sup>203</sup> W. H. Carothers and J. W. Hill, *J.A.C.S.*, 1932, 54, 1579.

same type. These results indicate the orientation of the crystal units in a lustrous fiber. A similar oriented fiber was obtained with ethylene sebacate, as well as with mixed polyesters and polyamides of the type derived from  $\epsilon$ -aminocaproic acid.

The polyoxymethylenes,<sup>204</sup> formed by the polymerization of formaldehyde, offer a very interesting example of the application of x-rays. The chemistry of these

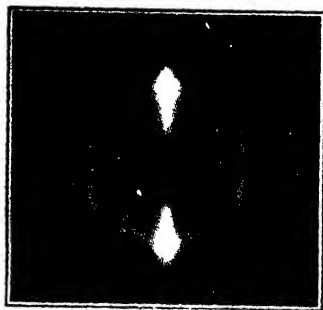


FIG. 40.  
X-Ray Diffraction Pattern of Stretched Chloroprene.<sup>a</sup>

<sup>a</sup> Courtesy W. H. Carothers. Photograph taken by A. W. Kenney.

substances has been studied exhaustively by Staudinger and his co-workers.<sup>205</sup> X-Ray examination of the lower crystalline polyoxymethylenes indicates that they are linear polymers comparable to the paraffins, i.e., a zig-zag chain structure. (See Fig. 42.)

The end groups of the chain-like molecules do not show definite characteristic features in the x-ray photograph. It is only the unit in the chain, and the distances of the chains from one another which are significant. Thus polyoxymethy-

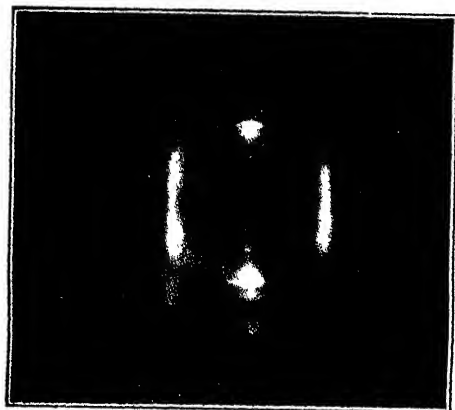


FIG. 41  
Stretched Bromoprene <sup>a</sup>

<sup>a</sup> Courtesy W. H. Carothers. Photograph taken by A. W. Kenney.

lene hydrate and polyoxymethylene dimethyl ether yield x-ray patterns which are almost identical.

The type of arrangement shown above is obtained only with relatively short polymers. In the case of polymers of greater molecular weight, which are as a rule insoluble, there is no definite intermolecular distance in the arrangement. The molecules in general are still oriented in parallel bunches, though they lie end to end without any definite arrangement.

<sup>204</sup> See Chapter 23.

<sup>205</sup> H. Staudinger, "Hochmolekularen organischen Verbindungen," 1932, 224, *et seq.*

It is characteristic of x-ray diffraction patterns obtained from very small particles that the lines of the photograph become broad and hazy as the particle size is reduced<sup>200</sup>. The case of colloidal gold is illustrative. Gold normally gives sharp lines and the lattice is cubic. When the metal is in the colloidal state, however, with a particle size corresponding to only about 20 atoms, diffuse lines are observed, though the cubic symmetry is retained. The same feature is observed

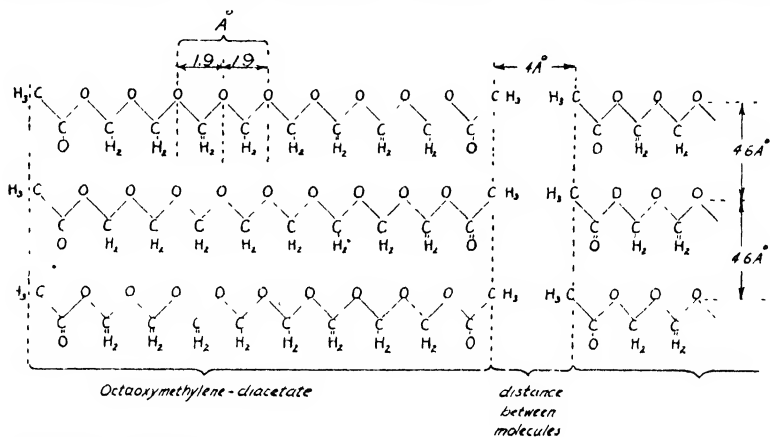


FIG. 42—The Probable Arrangement of Octa-oxyethylene Diacetate Molecules.

during the transformation from the amorphous to the crystalline state. The aggregates formed in the early stages of crystallization are very small, and hazy diffraction bands are produced. As the crystals develop the bands sharpen into the usual lines. This is true of the polyoxymethylene hydrate gel. Immediately after preparation there is a nearly complete random arrangement of the molecules and the rings are very diffuse. The appearance after 2 days is somewhat different. There is a definite pulling together of the molecules into ordered groups and as a result the diffraction lines become much sharper.

<sup>208</sup> See R. Zsigmondy, "Kolloidchemie," 3rd Ed., p. 387.

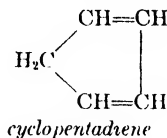
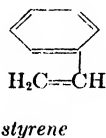
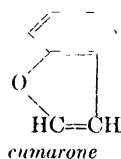
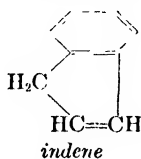
## Chapter 5

### Cumarone and Indene

Cumarone, indene and their homologues are the parent substances for the production of the so-called cumarone resins. Their occurrence and general reactions are summarized in this chapter.

Resins are produced from cumarone and indene by direct homo-polymerization in the presence of a catalyst such as sulphuric acid. As indicated by its structural formula, indene is a hydrocarbon possessing both olefinic and aromatic properties. In its high chemical reactivity and tendency to polymerize, indene is similar to styrene<sup>1</sup> and cyclopentadiene.<sup>2</sup> Cumarone is the oxygen analogue of indene.

The structural relationships can be seen as follows:



All of the compounds are, in effect, substituted ethylene derivatives<sup>3</sup>

In practice, separation of pure indene and cumarone is both difficult and expensive; hence, fractions of solvent naphtha (coal-tar distillate) rich in cumarone and indene are used as raw materials in resin manufacture, since polymerization readily occurs despite dilution by other compounds. For various reasons (one of which was the presence of other unsaturated, polymerizable substances in solvent naphtha) the first attempts at commercial manufacture of resins yielded dark sticky products of limited application. Methods of purification of the raw material and the technic of resinification have been so developed that light-colored, hard resins of manifold uses are now easily made. The present commercial cumarone resins are clean, nearly odorless products. They differ markedly from the offensive tars and acid sludges (obtained in the usual course of acid-refining of coal-tar naphtha) which, though containing resins, also include so many undesirable substances as to be practically useless.

#### CUMARONE

Cumarone is a water-white, oily liquid of peculiar odor, boiling at 172°C. and having a specific gravity of 1.096 at 15°. It is insoluble in water and volatile with

<sup>1</sup> See Chapter 11

<sup>2</sup> See Chapter 9

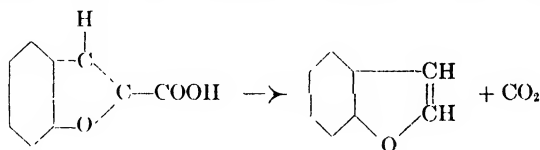
<sup>3</sup> See Chapter 51 for the effect of different substituent groups on the properties of compounds possessing the ethylene or vinyl grouping.

steam and is present in the fraction of coal-tar naphtha boiling between 168-175°, which is the source of cumarone for resin manufacture.

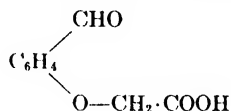
Kraemer and Spilker<sup>4</sup> isolated cumarone from a coal-tar fraction (boiling between 168° and 175°C) which had been treated with caustic alkalis and with acid. They brominated 1 kilogram of this material by the gradual addition of 450 grams of bromine while maintaining the temperature below 0°C., and obtained 80 grams of cumarone dibromide, which crystallized in prisms melting at 88-89°C. By prolonged boiling with alcoholic potash under reflux, the dibromide was converted to bromocumarone (m.p., 39°). From a solution of bromocumarone in 70 per cent alcohol, cumarone was regenerated by reduction with sodium amalgam.

Later, these same investigators<sup>5</sup> obtained cumarone by resinifying a crude coal-tar naphtha (b.p. 155-185°C) with sulphuric acid, destructively distilling the resins formed, and converting the cumarone in the 168-172° fraction into the picrate. They stated that this method of separating cumarone from hydrindene (indane), which occurs in the same fraction, is easier than separating the former directly from crude-tar naphtha. The method has been criticized by Burda and Sukacheva,<sup>6</sup> who, by using it, secured only 0.11 per cent yield of cumarone from a solvent naphtha boiling between 140° and 200°C.<sup>7</sup>

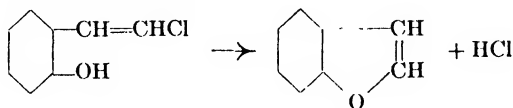
**Chemical Properties of Cumarone.** The name cumarone is unfortunate in that it suggests, quite erroneously, this substance is a ketone, whereas it is an unsaturated cyclic oxide. Cumarone has been synthesized by a number of methods, which are only of purely scientific interest. It was prepared by Fittig<sup>8</sup> by distilling cumarilic acid with lime, the reaction being represented thus:



Rössing<sup>9</sup> obtained cumarone by boiling o-aldehydephenoxyacetic acid



with anhydrous sodium acetate and acetic anhydride. Another procedure is the treatment of phenoxyacetaldehyde with glacial acetic acid and zinc chloride.<sup>10</sup> One synthesis of cumarone depends upon the elimination of hydrogen chloride from o-hydroxy-β-chlorostyrene by alkalis.<sup>11</sup>



<sup>4</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 78.

<sup>5</sup> G. Kraemer and A. Spilker, *Ber.*, 1900, 33, 2257; *J. C. S.*, 1900, 78 (1), 656.

<sup>6</sup> N. I. Burda and U. D. Sukacheva, *Ukrain. Khim. Zhur.*, 1931, 6, (Sci.), 169; *Chem. Abs.*, 1932, 26, 2192.

<sup>7</sup> This criticism must be considered carefully because of the uncertainty of the origin of the naphtha used by Burda and Sukacheva. If it was a commercial product some polymerization may have occurred previously and it is even possible that the normal traces of other hydrocarbons had been increased by the addition of residual fractions from other distillations.

<sup>8</sup> R. Fittig and G. Ebert, *Ann.*, 1883, 216, 168; *Ber.*, 1883, 16, 413; *Ann.*, 1884, 226, 354.

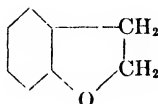
<sup>9</sup> A. Rössing, *Ber.*, 1884, 17, 3000.

<sup>10</sup> R. Stoerner, *Ber.*, 1897, 30, 1703.

<sup>11</sup> G. Komppa, *Ber.*, 1893, 26, 2969.

One of the characteristics of cumarone is the stability of its oxide ring system. This is not affected by potassium cyanide, by hot hydrochloric acid or by ammonia at 280°C. Cumarone is not decomposed by boiling aqueous or alcoholic potash, although concentrated alcoholic potash at 200° hydrolyzes it with rupture of the oxide ring.

The unsaturated character of cumarone is shown by its numerous addition reactions and by its power of additive polymerization. With bromine in the cold it readily forms a dibromide (m.p., 88-89°C.).<sup>12</sup> On hydrogenation, either catalytically or by sodium and boiling alcohol, the corresponding dihydride, dihydrocumarone,



results,<sup>13</sup> together with o-ethylphenol as a by-product. Cumarone combines with nitrous acid to yield nitrosites<sup>14</sup> and with hypochlorous acid to give a mixture of isomeric chlorohydrins. From the latter Boes<sup>15</sup> isolated a chlorohydrin (m.p. 123°C.) convertible by potassium hydroxide into cumarone glycol (m.p. 151°). Strong inorganic acids, including sulphuric, phosphoric, hydrobromic and hydriodic acids, polymerize cumarone, the products being of a resinous nature. By careful nitration with concentrated nitric acid, Stoermer and Richter<sup>16</sup> obtained a mixture of two isomeric nitrocumarones, an oxidation product and resinous substances. Oxidizing agents, such as bleaching powder and potassium permanganate react violently, the latter causing the formation of a resin.

Cumarone is distinguished by its stability at high temperatures. Kraemer and Spilker<sup>17</sup> found that 94 per cent of the compound remained unchanged after passage through a red-hot tube. The stability of cumarone and its homologues at high temperatures permits their formation in a number of pyrolytic reactions, and explains their occurrence among the products obtained by cracking higher-boiling phenols of primary coal-tar.<sup>18</sup> Cumarone results from the pyrolysis of cumarin at 860°C. and atmospheric pressure<sup>19</sup> and polymerized methyleumarones have been produced by the pyrolysis of hexahydrodiphenylene oxide.<sup>20</sup>

Cumarone forms a characteristic picrate (m.p. 102-103°C.),<sup>21</sup> and yellow, crystalline, unstable double compounds with 1,3,5-trinitrobenzene (m.p. of equimolecular addition product, 103.5-104°).<sup>22</sup>

**Polymerization of Cumarone.** The polymerization of cumarone has been studied less systematically than that of indene, but indications are that the mechanisms are similar. Much of the work, however, is rendered somewhat uncertain by the fact that investigators have used impure cumarone as the starting material.

<sup>12</sup> R. Fittig and G. Ebert, *Ann.*, 1883, 216, 169. G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 80. R. Stoermer and B. Kahlert, *Ber.*, 1902, 35, 1635.

<sup>13</sup> H. Alexander, *Ber.*, 1892, 25, 2409. M. Weger, *Z. angew. Chem.*, 1909, 22, 391. Molybdenum catalysts have been suggested for the hydrogenation of cumarone resins. See British Patent 247,586, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1927, 21, 643. H. Winter and G. Free, *Brennstoff-Chem.*, 1934, 15, 287; *Brit. Chem. Abs. B*, 1934, 914.

<sup>14</sup> M. Dennstedt and C. Ahrens, *Ber.*, 1895, 28, 1333.

<sup>15</sup> J. Boes, *Apoth. Ztg.*, 1908, 23, 153. *Chem. Zentr.*, 1908, 1, 1185. *J. C. S.*, 1908, 94 (1), 444.

<sup>16</sup> R. Stoermer and O. Richter, *Ber.*, 1897, 30, 2094.

<sup>17</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 78; *J. C. S.*, 1890, 58, 496.

<sup>18</sup> W. Gluud and P. K. Breuer, *Gas. Abhandl. Kenntnis Kohle*, 1918, 3, 238.

<sup>19</sup> N. A. Orlov and V. V. Tischenko, *Ber.*, 1930, 63, 2948; *Brit. Chem. Abs. A*, 1931, 233.

<sup>20</sup> N. A. Orlov and M. A. Belopolski, *Ber.*, 1929, 62, 1752; *Brit. Chem. Abs. B*, 1929, 806.

<sup>21</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 3276. Cf. British Patent 1422, 1890, to Chem. Fabrik. A.-G.; *J. S. C. I.*, 1890, 9, 546. German Patent 53,792, 1890; *Chem. Zentr.*, 1891, 1, 111.

<sup>22</sup> J. J. Sudborough and S. H. Beard, *J. C. S.*, 1911, 99, 209, 215.

Kraemer and Spilker<sup>23</sup> found that when a solution of cumarone in benzene is shaken with sulphuric acid the greater part of it is converted into a resin soluble in benzene and the remainder separates as a brown insoluble powder. If 80 per cent sulphuric acid is used as polymerizing agent the soluble resin is formed almost exclusively. The yield of the insoluble resin increases with the concentration of the acid; with 95 per cent sulphuric acid, the insoluble resin is formed quantitatively. A soluble resin melting at 107-108°C. and having a specific gravity of 1.25 had a molecular weight corresponding to a tetramer of cumarone,  $(C_8H_6O)_4$ .<sup>24</sup> When heated at 300-350°, this resin furnished a distillate consisting mainly of cumarone together with some phenol, ethylbenzene, and small quantities of o-ethylphenol, toluene, and dihydrocumarone.

Insoluble resins formed by the action of concentrated sulphuric acid were found by Kraemer and Spilker<sup>25</sup> to contain combined sulphur. On destruc-

FIG. 43

X-Ray Diffraction Pattern of a Cumarone Resin (Cumar) Copper Radiation.



Courtesy H. V. Anderson

tive distillation these substances yielded sulphur, sulphur dioxide, hydrogen sulphide and practically the same products as those obtained from the soluble resins. According to Kraemer and Spilker, the polymerization of cumarone proceeds with little rise in temperature but that of indene is attended with a considerable evolution of heat.

Besides sulphuric acid, a number of other agents polymerize cumarone to substances of a resinous nature. Heusler<sup>26</sup> noted that anhydrous aluminum chloride converted cumarone into a soluble resin. Stein<sup>27</sup> observed that aluminum chloride, phosphorus oxychloride and stannic chloride (particularly the latter) cause resinification. On the other hand, silicon tetrachloride, zinc chloride, hydrogen chloride, sulphur monochloride, and potassium hydrogen sulphate exert little or no action. Cumarone, exposed to air, undergoes autoxidation and subsequent polymerization.

From the meager data available it appears that the resinification of cumarone by catalysts is a purely additive polymerization, although an excess of concentrated sulphuric acid effects some sulphonation.

<sup>23</sup> G. Kraemer and A. Spilker, *Ber.*, 1900, 33, 2257; *JCS*, 1900, 78 (1), 656.

<sup>24</sup> R. Stoermer (*Ann.*, 1900, 312, 237) obtained, during the preparation of cumarone by the dehydration of phenoxyacetaldehyde, a polymer of cumarone, having a molecular weight corresponding to  $(C_8H_6O)_4$ , a yellow-brown powder melting at 80-100°C. This polymer was very soluble in ether, benzene and chloroform but less soluble in alcohol.

<sup>25</sup> G. Kraemer and A. Spilker, *Ber.*, 1901, 34, 1887.

<sup>26</sup> F. Heusler, *Z. angew. Chem.*, 1896, 9, 318.

<sup>27</sup> E. Stein, *Z. angew. Chem.*, 1919, 32, 246; *Chem. Abs.*, 1920, 14, 641.

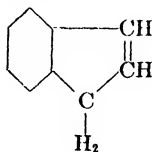
The name "paracumarone"<sup>228</sup> has been applied to the benzene-soluble resins obtained by the controlled polymerization of cumarone. This material, which is of variable melting point, is soluble in many of the ordinary organic solvents (with the exception of alcohol) and is stable towards alkalis and most acids.

**Homologues of Cumarone.** Isomeric methylcumarones were found by Stoermer and Boes<sup>229</sup> in the fraction of coal-tar distillate boiling between 185° and 200°C. By treating a coal-tar fraction (boiling range 185-195°C.) with sulphuric acid they prepared polymers of methylcumarone which decomposed, on heating, into hydrindene and methylcumarone, together with the corresponding cresols.

Stoermer and Boes also isolated dimethylcumarones from the fraction of tar oils boiling between 215° and 225°. These compounds were not resinified by concentrated sulphuric acid.<sup>230</sup>

### INDENE

**Occurrence of Indene.** Indene is a colorless oily liquid boiling at 182°C., solidifying at -2° and possessing a specific gravity of 1.0002 at 15°C.<sup>231</sup> It is an important constituent of certain fractions of tars and naphthas obtained in the



high-temperature carbonization of coal and similar bituminous materials. From 10 kilograms of a coal-tar naphtha, boiling between 176° and 180°C., Kraemer and Spilker<sup>232</sup> obtained 3 kilograms of crude indene. Weissgerber<sup>233</sup> used a 175-185° fraction of solvent naphtha as a source of pure indene. Indene is present to a much smaller extent in the so-called primary tars produced by the carbonization of bituminous substances at lower temperatures.<sup>234</sup> This is attributed to the fact that indene, like most polynuclear aromatic hydrocarbons, is essentially a product of high-temperature pyrolytic reactions.<sup>235</sup> Accordingly, indene (and other cyclic hydrocarbons) is produced during the high-temperature pyrolysis of many organic substances, notably in the thermal decomposition of acetylene-hydrogen mixtures,<sup>236</sup> and of the higher-boiling phenols of primary tar.<sup>237</sup> Pyrolysis of desulphurized (Persian) natural gas, at 850° and a pressure of 20 pounds per square inch, yielded about 5 per cent styrene and 2 per cent indene.<sup>238</sup> Two carbureted water-gas tars examined by Brown and Howard<sup>239</sup> possessed an indene content of 1.9 and 1.2 per cent, respectively, of the total volume of tar.

<sup>228</sup> Since, in all probability, a whole series of polymerized cumarones exists, these resins should be more properly designated by the term "polycumarone." The ordinary cumarone resin of commerce is frequently called paracumarone, though actually a mixture of polymerized cumarones and indenenes. The name paracumarone was applied by G. Kraemer and A. Spilker (*Ber.*, 1890, 23, 78) to the resin produced by polymerizing cumarone with sulphuric acid.

<sup>229</sup> R. Stoermer and J. Boes, *Ber.*, 1900, 33, 3013; *J.C.S.*, 1901, 80 (1), 31; *J.S.C.I.*, 1900, 19, 1098.

<sup>230</sup> A large number of cumarone homologues has been synthesized by R. Stoermer and his collaborators; see *Ber.*, 1897, 30, 1700; *Ann.*, 1900, 312, 237; 1900, 313, 79.

<sup>231</sup> A. Spilker and A. Dombrowsky, *Ber.*, 1900, 42, 573.

<sup>232</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 3276.

<sup>233</sup> R. Weissgerber, *Ber.*, 1909, 42, 569.

<sup>234</sup> R. Weissgerber, *Brennstoff-Chem.*, 1924, 5, 208; *Chem. Abs.*, 1924, 18, 3705; *Ber.*, 1928, 61, 2111; *Brit. Chem. Abs. B*, 1928, 917.

<sup>235</sup> See Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, 81, 82, 180.

<sup>236</sup> R. Meyer and W. Meyer, *Ber.*, 1918, 51, 1571.

<sup>237</sup> W. Glud and P. K. Breuer, *Gen. Abhandl. Kenntnis Kohle*, 1918, 3, 238.

<sup>238</sup> S. F. Birch and E. N. Hague, *Ind. Eng. Chem.*, 1934, 26, 1008.

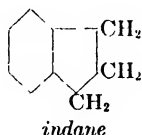
<sup>239</sup> R. L. Brown and R. D. Howard, *Ind. Eng. Chem.*, 1923, 15, 1147.



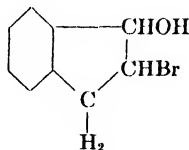
Although coal-tar naphthas serve as the principal sources of indene for technical purposes, there are indications that coal gas and carbureted water-gas are potential sources of large amounts of both indene and styrene. Indene and other reactive hydrocarbons are appreciably volatile in freshly-made gas, and are carried forward in the gas stream, later polymerizing to form gummy deposits in the gas-handling equipment. The indene content of freshly-made carbureted water-gas may exceed 100 grams per 1000 cubic feet.<sup>40</sup> A survey of the gas industry in the United States, according to Brown,<sup>41</sup> revealed that 6.5-10 million gallons of drip oil were produced annually which contained large proportions of styrene and indene. The oily condensate collecting in gas mains is also a potential source of indene and allied substances. Examination of representative samples of the oily condensate (drip oil) from carbureted water-gas mains revealed that the dried liquid contained up to 35 per cent indene and 15 per cent styrene. Fractions containing 75 per cent indene were obtainable by rough fractionation.

Indene has been prepared by a number of syntheses, none of which, however, appears to be of industrial significance.<sup>42</sup>

**Chemical Properties of Indene.** The olefinic nature of indene is indicated by numerous addition reactions. Reduction by sodium in boiling alcohol,<sup>43</sup> or by hydrogen and a nickel catalyst at 200°C.,<sup>44</sup> results in the addition of 2 hydrogen atoms to the indene molecule. Hydrindene (indane), a stable hydrocarbon, is thus obtained:



With halogens, indene readily forms the corresponding dihalides (dihalogenoindanes). Indene dibromide, prepared by bromination of indene in carbon tetrachloride solution at 0°C., is a crystalline solid<sup>45</sup> (m.p. 31.5-32.5°C.)<sup>46</sup> which is readily converted by the action of boiling water or steam into the corresponding hydroxybromide (m.p. 130.5°). This hydroxybromide, which has proved useful in the identification of indene,<sup>47</sup> possesses the structure:



Nitration of dibromoindane yields a yellow sticky resin.<sup>48</sup> Chlorination of indene

<sup>40</sup> A. L. Ward, C. W. Jordan, and W. H. Fulweiler, *Ind. Eng. Chem.*, 1932, 24, 969, 1238. See also C. W. Jordan, A. L. Ward and W. H. Fulweiler, *Ind. Eng. Chem.*, 1934, 26, 947, 1028.

<sup>41</sup> R. L. Brown, *Ind. Eng. Chem.*, 1928, 20, 1178; *Am. Gas. Assoc. J.*, 1922, 159, 327; *J.S.C.I.*, 1922, 41, 669A. The problem of gum-formation in manufactured gas is discussed by W. H. Fulweiler, *Am. Gas. Assoc. Proc.*, 1932, 14, 838; *Gas Age-Record*, 1932, 70, 453; *Gas J.*, 1932, 200, 570; *Chem. Abs.*, 1933, 27, 3318. J. A. Perry, *Gas Age-Record*, 1933, 71, 387; *Chem. Abs.*, 1933, 27, 3318. R. N. Wenzel, *Gas Age-Record*, 1933, 71, 413; *Chem. Abs.*, 1933, 27, 3318. R. L. Brown, *Ind. Eng. Chem.*, 1925, 17, 920.

<sup>42</sup> See, e.g., F. S. Kipping and H. Hall, *J.C.S.*, 1900, 77, 468. W. H. Perkin, Jr. and G. Révay, *Ber.*, 1893, 26, 2251; *J.C.S.*, 1894, 65, 228.

<sup>43</sup> The chemistry of indene has been reviewed by C. Courtot, *Rev. gen. sci.*, 1923, 34, 607; *Chem. Abs.*, 1924, 18, 2690.

<sup>44</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 3281. M. Padon and U. Fabris, *Atti accad. Lincei*, 1908, (5) 17 (1), 111; *J.C.S.*, 1908, 94, 255; *Gazz. chim. ital.*, 1909, 39, 327; *Chem. Abs.*, 1909, 3, 1868.

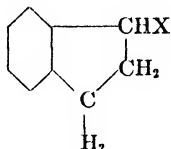
<sup>45</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 3279.

<sup>46</sup> A. Spilker and A. Dombrowsky, *Ber.*, 1909, 42, 573.

<sup>47</sup> R. L. Brown and R. D. Howard, *Ind. Eng. Chem.*, 1923, 15, 1147.

<sup>48</sup> W. Borsche and A. Bodenstein, *Ber.*, 1926, 59, 1915.

gives a liquid dichloride which can be hydrolyzed by boiling aqueous alcohol to the corresponding hydroxychloride.<sup>49</sup> Indene combines readily with hydrogen halides (except hydrogen fluoride) with the formation (in good yields) of halogenoindanes of the general formula:

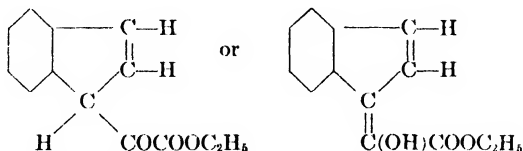


(X = Cl, Br, or I)

The hydrochloride (chloroindane) may be made by saturating indene with dry hydrogen chloride at 0°. <sup>50</sup> However, the corresponding bromo- and iodoindanes, although obtainable in good yields, cannot be purified and, unless immediately used, lose hydrogen halide and form polymers of indene.<sup>51</sup> Hydrogen fluoride exerts a strong polymerizing action on indene.

Pure indene on exposure to air rapidly absorbs oxygen and is converted into a substance insoluble in alcohol and not distillable with steam.<sup>52</sup> It can be oxidized by aqueous potassium permanganate to 1,2-dihydroxyindane, and subsequently to homophthalic acid (2-carboxyphenylacetic acid).<sup>53</sup> Like other unsaturated hydrocarbons, indene yields a nitrosite with nitrous acid and forms a double compound with mercuric sulphate.

The methylene group of the five-membered ring of the indene molecule is capable of undergoing a series of characteristic reactions which markedly accentuate the similarity of indene to cyclopentadiene and differentiate it from cumarone. Thus, when indene is treated with sodamide at 110-115°C., one hydrogen atom of the reactive methylene group is displaced by sodium to yield sodium indene,<sup>54</sup> a substance which can be used in the preparation of pure indene. The reaction of sodium indene with benzyl chloride<sup>55</sup> yields benzyhindene (m.p. 33-34°). Like cyclopentadiene, indene can react with aldehydes in alkaline media, and its reaction with benzaldehyde has been proposed as a basis of a method for the estimation of indene.<sup>56</sup> Condensation of indene with ethyl oxalate in the presence of sodium ethoxide at ordinary temperatures produces, after acidification, ethyl indeneoxalate,<sup>57</sup> a crystalline orange-red substance (m.p. 85°C.) having the constitution:



<sup>49</sup> A. Spilker, *Ber.*, 1893, 26, 1541. C. Courtot, Fayet and Parant, *Compt. rend.*, 1928, 186, 371, *Chem. Abs.*, 1928, 22, 1352.

<sup>50</sup> C. Courtot and A. Dondelinger, *Ann. chim.*, 1925, (10) 4, 231; *Chem. Abs.*, 1926, 20, 755.

<sup>51</sup> C. Courtot and A. Dondelinger, *Ann. chim.*, 1925, (10) 4, 345; *Chem. Abs.*, 1926, 20, 756.

<sup>52</sup> M. Weger and A. Billmann, *Ber.*, 1903, 36, 640. Resins for use as components of black printing colors have been made by oxidizing tars or high-boiling tar oils (German Patent 364,830, 1920, to Rütgerswerke A.-G.; *J.S.C.I.*, 1923, 42, 614A).

<sup>53</sup> F. Heusler and H. Schieffer, *Ber.*, 1899, 32, 29.

<sup>54</sup> R. Weissgerber, *Ber.*, 1909, 42, 569.

<sup>55</sup> R. Weissgerber, *Ber.*, 1911, 44, 1436. Cf. J. Thiele and A. Bahner, *Ann.*, 1906, 347, 266; *J.C.S.*, 1906, 90 (1), 589. The preparation of methyindene is described by W. Marckwald (*Ber.*, 1900, 33, 1504). Alkylated or arylated indenenes, such as benzyhindene, have been suggested as linseed-oil substitutes (German Patent 305,515, 1917, to Farbenfabriken vorm. F. Bayer & Co; *J.S.C.I.*, 1920, 39, 165A).

<sup>56</sup> M. Weger and A. Billmann, *loc. cit.* W. Marckwald, *Ber.*, 1895, 28, 1503. J. Thiele, *Ber.*, 1900, 33, 3395.

<sup>57</sup> W. Wislicenus, *Ber.*, 1900, 33, 771. J. Thiele, *Ber.*, 1900, 33, 851.

These characteristic reactions of the methylene group provide methods of separating indene from cumarone.

With an aqueous solution of picric acid, indene readily yields a crystalline precipitate of indene picrate (m.p. 98°C.).<sup>58</sup> This compound, which has proved useful in the partial separation of indene from crude materials, is soluble in benzene and alcohol and may be decomposed into its constituents by steam distillation.

**Separation of Indene from Solvent Naphtha.** For the isolation of indene from complex mixtures, such as coal-tar fractions, Kraemer<sup>59</sup> used the picrate-precipitation method as follows: The fraction of crude benzol boiling at 176-182°C. is treated with sufficient picric acid to combine with all the unsaturated hydrocarbons present. The resulting crystalline precipitate, containing the picrates of naphthalene and cumarone, as well as of indene, is subjected to steam distillation. Indene picrate is decomposed and the liberated indene distils over. From 10 kilograms of crude naphtha (b.p. 176-182°), 3 kilograms of crude indene were obtained by this procedure. However, not only is the method somewhat dangerous because of the explosive nature of these picrates, but the resulting indene is far from pure.

A more practical method for the preparation of pure indene, developed by Weissgerber,<sup>60</sup> consists in converting crude indene into sodium indene, separating the unreacted material (cumarone, naphthalene, styrene) by distillation, and decomposing the sodium indene residue with water. A crude naphtha fraction boiling at 175-185°C. is first freed from phenols and bases and treated with the stoichiometric amount of metallic sodium. Ammonia is passed through the mixture, which is thoroughly stirred and maintained at 120-130° for 5-6 hours with the exclusion of moisture and air from the apparatus. If organic bases, such as pyridine or aniline, are not first removed, a temperature of 100-105° is sufficient. The product is then distilled under reduced pressure (20-30 mm.), most of the unreacted material being volatile at about 100°. The residual dark amorphous mass is easily decomposed by water, and indene in a pure condition is isolated by steam distillation. This procedure, with slight modification, has been successfully employed by other investigators.<sup>61</sup>

Sodium indene can be obtained also from coal-tar fractions by treatment with metallic sodium at temperatures above 130°C. in the absence of ammonia. Organic bases assist this reaction but do not increase the yield.<sup>62</sup>

Separation of indene from cumarone may be effected also by converting the former into compounds in which the methylene group is the point of attack (e.g., ethyl indeneoxalate). Such derivatives, however, are not easily reconverted into indene. The hydroxybromides of indene, obtained by steam distillation of the dibromide, have been employed for separating indene from styrene.<sup>63</sup>

Another method of isolating indene from tar oils is that developed by Kahl.<sup>64</sup> This consists in fractionating the crude oils and cooling to -25°C. those fractions containing 80 per cent or more of indene. At this temperature indene of a high degree of purity crystallizes and the liquid portion is removed by centrifuging. Fractions containing less than 80 per cent indene can be cooled until partial

<sup>58</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 3276; 1900, 33, 2262. R. L. Brown and H. G. Berger, *Ind. Eng. Chem.*, 1924, 16, 917.

<sup>59</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 3276.

<sup>60</sup> R. Weissgerber, *Ber.*, 1909, 42, 569. German P. 205,465, 1908, to Ges. für Teerverwertung m b H; *J.S.C.I.*, 1909, 28, 84.

<sup>61</sup> See, C. Courot and A. Dondelinger, *Ann. chim.*, 1925, (10) 4, 231; *Chem. Abs.*, 1926, 20, 755.

<sup>62</sup> R. Weissgerber, German P. 209,694, 1908, to Ges. für Teerverwertung; *J.S.C.I.*, 1909, 28, 649. Cf. German P. 205,465, 1908; *J.S.C.I.*, 1909, 28, 84.

<sup>63</sup> R. L. Brown and R. D. Howard, *Ind. Eng. Chem.*, 1923, 15, 1147.

<sup>64</sup> L. Kahl, U. S. P. 1,943,078, Jan. 9, 1934; *Chem. Abs.*, 1934, 28, 1846. British P. 405,900, 1933, to Rutgerswerke-A.-G.; *Brit. Chem. Abs. B.*, 1934, 313. French P. 768,733, 1934; *Chem. Abs.*, 1935, 29, 482. German P. 590,233, 1934, addn. to 589,560, 1933; *Chem. Abs.*, 1934, 28, 2373, 2732.

solidification takes place, the solid portion separated, remelted, and treated as described above.

**Polymerization of Indene.** The polymerization of indene takes place under the influence of light or heat, and more readily in the presence of a variety of catalysts, to yield a series of products, the higher members of which are resins. In this respect it shows a marked similarity to styrene.<sup>65</sup> Although concentrated sulphuric acid is employed almost exclusively as the catalyst in the polymerization of cumarone and indene to yield commercial resins, other catalysts, such as tin tetrachloride, are even more efficacious. Polymerization of indene is strongly exothermic and for this reason reaction is usually effected in liquid diluents with rapid cooling and agitation. The use of high pressures (2000-12,000 atmospheres) is suggested by Bridgman and Conant.<sup>66</sup> Not only does indene homo-polymerize, but, like styrene and the vinyl esters and ethers, it can hetero-polymerize with compounds such as  $\alpha$ ,  $\beta$ -dicarboxylic acids, or their anhydrides (e.g., maleic anhydride). The products thus obtained are used as dispersing, emulsifying and finishing agents for textiles.<sup>67</sup>

**Polymerization of Indene by Heat.** Indene undergoes little change when heated at 115-118°C. in the dark in an atmosphere of nitrogen, but after 96 hours at 190-200°C., it is transformed into a colophony-like mass which consists mainly of a mixture of polyindenes, including  $(C_9H_8)_8$  and  $(C_9H_8)_{12}$ , according to Stobbe and Färber.<sup>68</sup> By heating indene in a sealed tube at 180-200°C., for 100 hours, Stobbe and Zschoch<sup>69</sup> obtained a yellow, benzene-soluble resinous mass. A yellow amorphous powder having a molecular weight corresponding to a tetraindene,  $(C_9H_8)_4$ , was obtained by Bruson<sup>70</sup> by heating indene in a sealed tube at 260° for 25 hours. This tetraindene, which could not be crystallized, melted indefinitely at 100-110°.

Brown<sup>71</sup> found that, at 300-500°C., indene vaporized in nitrogen polymerized rapidly but when oxygen was present it underwent rapid oxidation. Whitby and Katz<sup>72</sup> showed that a series of polyindenes is produced during thermopolymerization of indene in sealed tubes. At a given temperature the molecular weight of the product was found to rise as the proportion of indene transformed increased, but the ultimate molecular size attained (when polymerization was substantially complete) was lower at higher temperatures. Thus, after 21 days at 200°C., when 96 per cent of the indene had polymerized, the molecular weight was 676, but at 178°C. after 30 days, 82 per cent of the indene had polymerized to a product with an average molecular weight of 886. Fractional precipitation of the materials from ether solution by the addition of alcohol yielded a series of polymers having melting points proportional to their molecular weights. Comparison of these thermopolymers with products obtained by the use of catalysts, such as sulphuric acid, showed that the polymers of indene, no matter by which of the known methods they are produced, form a regular and unbroken series. Another fact brought out by Whitby and Katz is that all the polyindenes show the same degree of unsaturation, namely, that represented by the addition of 2 atoms of bromine per molecule. Hence these investigators concluded that all the polyindene molecules, no matter what their size, contain 1 double bond.

<sup>65</sup> However, the polyindenes of highest molecular weight are relatively simple molecules when compared with the gigantic macromolecules formed in the polymerization of styrene. See Chapter 11

<sup>66</sup> P. W. Bridgman and J. B. Conant, U. S. P. 1,952,116, Mar. 27, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3415.

<sup>67</sup> German P. 571,665, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4419. See also Chapter 4 for a discussion of hetero-polymerization

<sup>68</sup> H. Stobbe and E. Farber, *Ber.*, 1924, 57, 1838; *Chem. Abs.*, 1925, 19, 492.

<sup>69</sup> H. Stobbe and F. Zschoch, *Ber.*, 1927, 60, 457.

<sup>70</sup> H. A. Bruson, *Ber.*, 1927, 60, 1094.

<sup>71</sup> R. L. Brown, *Ind Eng Chem.*, 1925, 17, 920.

<sup>72</sup> G. S. Whitby and M. Katz, *J.A.C.S.*, 1928, 50, 1160; *Can. J. Research*, 1930, 4, 344, *Chem. Abs.*, 1931, 25, 3988.

By fractional precipitation of the polymeric material formed by heating indene at 200°C. for 8 days, Whitby and Katz obtained the fractions indicated in Table 16.

TABLE 16.—*Fractions of Polymerized Indene.*

Fraction	1	2	3	4	5
M. P. °C. ....	185–188	165–167	139–142	100–102	88–90
Average Mol. Weight. .	948	787	594	491	438

**Photopolymerization of Indene.** Transformation of indene to resins in ultraviolet light was noted by Guntz and Minguin.<sup>75</sup> According to Stobbe and Färber,<sup>74</sup> photopolymerization of pure indene in an atmosphere of nitrogen at 20°C. follows a normal, non-autocatalytic course, which is preceded by an induction period. Exposure to sunlight for a year yielded small quantities of resinous polymers,  $(C_9H_8)_8$  and  $(C_9H_8)_{10}$ . The formation of these polymers is accelerated by the presence of a trace of air.

**Catalytic Polymerization of Indene.** Sulphuric acid exerts a strong polymerizing action on indene (or its solutions), the degree of polymerization depending upon the concentration of the acid. Earlier workers in this field failed to realize the cumulative nature of the reaction and attempted to characterize as chemical individuals the complex mixture of products thus formed. Kraemer and Spilker<sup>76</sup> obtained a resinous polymer of high molecular weight (m.p. 210°C.) by treating a 20 per cent solution of indene in benzene with 15–20 per cent of concentrated sulphuric acid. This resin, to which the name paraindene was assigned, was later found to be heterogeneous and to have a variable molecular weight and melting point. Marcusson<sup>75</sup> made resins of various characteristics by polymerizing indene in benzene solution with different concentrations of sulphuric acid. By using concentrated sulphuric acid, a polymer was formed which melted at 210° and was insoluble in ether. On the other hand, diluted acid or smaller amounts of concentrated acid resulted in a mixture of products, one melting at 165°C., soluble in ether but insoluble in ether-alcohol, and another melting at 100°C. and soluble in ether-alcohol. Weger<sup>77</sup> made what he considered to be a tetramer of indene (to which he also assigned the name paraindene) by shaking a benzene solution of indene with a small proportion of concentrated sulphuric acid. By treating indene with concentrated sulphuric acid in the cold, Bruson<sup>78</sup> prepared a white amorphous product melting at 212–214°C. and having an apparent molecular weight corresponding to  $(C_9H_8)_{11}$  or  $(C_9H_8)_{12}$ . This material was similar to the paraindene of Kraemer and Spilker. The influence of various concentrations of sulphuric acid on the polymerization of indene was studied by Stobbe and Färber.<sup>79</sup> Dilute sulphuric acid (as well as other dilute mineral acids) polymerizes indene almost exclusively to the dimer. With aqueous sulphuric acid of 60 per cent strength and higher, diindene is formed as well as higher polymers. By treating undiluted indene with concentrated sulphuric acid in the cold, Stobbe and Färber obtained polymers with molecular weights lying between values required for  $(C_9H_8)_{10}$  and  $(C_9H_8)_{20}$ . These substances, which were white, amorphous, odorless powders having melting points in the range of 220–280°C., were called metaindene. The metaindene

<sup>75</sup> A. Guntz and J. Minguin, *Compt. rend.*, 1911, 152, 373; *J.C.S.*, 1911, 100 (2), 241. M. Weger and A. Billmann, *Ber.*, 1903, 36, 642. G. Ciamician and P. Silber, *Ber.*, 1913, 46, 420.

<sup>74</sup> H. Stobbe and E. Färber, *Ber.*, 1924, 57, 1838. Two arc lamps were used as source of illumination.

<sup>76</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 3278; 1900, 33, 2260.

<sup>75</sup> J. Marcusson, *Chem.-Ztg.*, 1919, 43, 83, 109, 122; *Chem. Abs.*, 1919, 13, 2807.

<sup>77</sup> M. Weger, *Z. angew. Chem.*, 1909, 22, 845. M. Weger and A. Billmann, *Ber.*, 1903, 36, 643.

<sup>78</sup> H. A. Bruson, Dissertation, Zürich, 1926, 60.

<sup>79</sup> H. Stobbe and E. Färber, *Ber.*, 1924, 57, 1838.

of Stobbe and Färber consists of a mixture of indene polymers of molecular weights somewhat higher than those of the so-called paraindene of Kraemer and Spilker.

Besides sulphuric acid, a number of other mineral and organic acids polymerize indene to varying degrees. Anhydrous hydrogen fluoride is a strong polymerizing agent and converts indene to a resin. As previously mentioned, other hydrogen halides combine additively with indene but the resulting bromo- and iodoindanes are unstable and tend to form resins with elimination of hydrogen halide.<sup>80</sup> On the other hand, warm dilute mineral acids, such as dilute hydrochloric and sulphuric acid, dimerize indene. A similar polymerization to diindene takes place, though more slowly, with weaker acids, such as phosphoric acid<sup>81</sup> and warm glacial acetic acid.<sup>82</sup> Dimerization can also be induced by concentrated aqueous zinc chloride solution or a 30 per cent solution of aluminum chloride in water.<sup>83</sup>

Indene is converted by a solution of iodine in aqueous potassium iodide into polymers of high molecular weight, but partial iodination also occurs. Stobbe and Färber<sup>84</sup> isolated an iodododecaindene,  $C_{108}H_{95}I$ , which melted at 200-210°C. with decomposition.

As mentioned before, polymerization of indene is catalyzed by a number of anhydrous metallic halides, including stannic chloride, antimony penta- and trichlorides, titanium tetrachloride and boron trichloride. Of these catalysts, stannic chloride and antimony pentachloride appear to be so active that inert diluents are necessary. Bruson<sup>85</sup> polymerized pure indene in chloroform solution by anhydrous stannic chloride at 10°C. Reaction is complete in 5-10 minutes and the product is a white, amorphous, non-crystalline powder, melting at 248-250° and having a molecular weight (in benzene solution) of 2900-3000, corresponding to  $(C_9H_8)_{32}$  to  $(C_9H_8)_{36}$ . This polymer is soluble in benzene, chloroform, carbon bisulphide, and pyridine, but only very slightly soluble in alcohol, acetone, and ether. The polyindenes obtained by the action of stannic chloride have been studied by Staudinger and his collaborators.<sup>86</sup> The influence of the concentration of indene in benzene solution on the yield and character of the polyindenes formed by the same amount of stannic chloride (2 per cent by volume of indene) at 5° is shown in Table 17.

TABLE 17.—*Polymerization of Indene by Stannic Chloride in Benzene Solution at Various Concentrations*

Concentration of Indene in Benzene Solution, %	Yield of Polyindenes, %	Characteristics of Polyindenes	
		Mol. Wt	Softening Point, °C
50	100	3670-3850	220
10	80	3240-3470	205
1	50	2350-2300	195

A number of experiments on the polymerization of indene in toluene solution (20 grams of indene in 250 cc. of toluene) at different temperatures, with the same amounts of stannic chloride as polymerizing agent, showed that lower temperatures favor the formation of materials of high molecular weights. The results of these experiments, which were all of 8 hours duration and in which the yield of polyindenes was in every case almost quantitative, are given in Table 18.

<sup>80</sup> C. Courtot and A. Dondelinger, *Ann. chim.*, 1925, (10) 4, 345; *Chem. Abs.*, 1926, 20, 756; *Compt. rend.*, 1924, 179, 1168; *Chem. Abs.*, 1925, 19, 827.

<sup>81</sup> H. Stobbe and E. Färber, *Ber.*, 1924, 57, 1838.

<sup>82</sup> R. Weissgerber, *Ber.*, 1911, 44, 1438.

<sup>83</sup> H. Stobbe and E. Färber, *Ber.*, 1924, 57, 1838.

<sup>84</sup> H. Stobbe and E. Färber, *loc. cit.*

<sup>85</sup> H. A. Bruson, Dissertation, Zürich, 1925, 61, 65.

<sup>86</sup> H. Staudinger, A. A. Ashdown, M. Brunner, H. A. Bruson and S. Wehrli, *Helv. Chim. Acta*, 1929, 12, 934. H. Staudinger, H. Johnner and V. Wiedersheim, *ibid.*, 1929, 12, 958. H. Staudinger, H. Johnner, G. Schiemann and V. Wiedersheim, *ibid.*, 1929, 12, 962; *Chem. Abs.*, 1930, 24, 612.

TABLE 18.—*Polymerization of Indene by Stannic Chloride in Toluene Solution at Various Temperatures.*

Temperature of Polymerization, °C.	Mean Molecular Weight in Toluene
– 80	3570
– 20	3270
+ 50	1190
+110	1540

All the polyindenes investigated by Staudinger and his collaborators were amorphous and hemicolloidal<sup>87</sup> in character.

Whitby and Katz<sup>88</sup> studied the polymerization of indene in chloroform solution by antimony pentachloride and stannic chloride, respectively. The resulting white amorphous products were fractionally precipitated by alcohol from benzene solution. Bromine-absorption tests (24 hours in dark in chloroform solution with 0.07*N* bromine in chloroform) showed that all fractions were unsaturated and absorbed 2 bromine atoms per molecule. Some of their results are shown in Table 19.

TABLE 19 —*Polyindene Polymerized by Stannic Chloride in Chloroform.*

Fraction	Mol Wt	M.P., °C	Bromine Absorption, Atoms per Molecule
1	3320	261-265	2.43
2	2785	247-250	2.06
3	2560	236-241	2.12
4	2295	231-235	1.97
5	1990	219-223	1.85
6	1568	198-201	2.19
7	952	164-167	1.93

Oxygen and certain unstable oxygenated derivatives of the peroxide type appear to catalyze the transformation of indene to resins.<sup>89</sup> An ozonized mixture of disobutylenes is an example of the latter type.<sup>90</sup> According to Ward, Jordan and Fulweiler,<sup>91</sup> the formation of gum from indene fractions is catalyzed by oxygen (especially in the presence of mercaptans) and is inhibited by phenols. On treatment with perbenzoic acid, indene yields both oxygenated and polymerized derivatives.<sup>92</sup> For the polymerization of indene Brusson<sup>93</sup> suggested the use of an aryldiazonium fluoroborate, e.g., phenyldiazonium fluoroborate,  $C_6H_5-N_2BF_4$ .

**Properties of Polyindenes.** As already stated, the polymerization products of indene form a series, their melting points rising uniformly with increasing molecular weight. Dielectric constants and refractive indices of the polymers also vary uniformly with increasing molecular weight.<sup>94</sup> Employment of such catalysts as sulphuric acid generally furnishes a mixture of polymers containing upwards of 50 members of the polymeric series. Although a rough fractionation may be effected, e.g., by fractional precipitation from solution, it is almost impossible to separate chemical individuals from such a complex mixture. Only dundene has been actually isolated in a relatively pure condition. The mixture of polymers is conveniently classified under the generic name of *polyindene*. The latter is a white powdery substance of a hemicolloidal character, the lower members being

<sup>87</sup> As opposed to eu colloidal. See Chapter 4 for discussion of colloidal properties of polymers in general.

<sup>88</sup> G. S. Whitby and M. Katz, *J. A. C. S.*, 1928, 50, 1166.

<sup>89</sup> H. Staudinger and L. Lautenschlager, *Ann.*, 1931, 488, 1; *Chem. Abs.*, 1931, 25, 5138.

<sup>90</sup> R. C. Houtz and H. Adkins, *J. A. C. S.*, 1931, 53, 1058.

<sup>91</sup> A. L. Ward, C. W. Jordan and W. H. Fulweiler *Ind. Eng. Chem.*, 1932, 24, 1238.

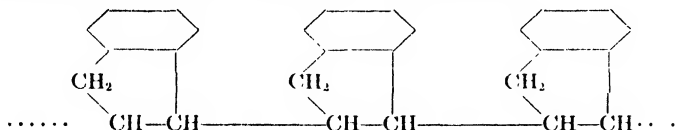
<sup>92</sup> K. H. Bauer and O. Bahr, *J. prakt. Chem.*, 1929, 122, 201; *Chem. Abs.*, 1930, 24, 60.

<sup>93</sup> H. A. Brusson, U. S. P. 1,892,101, Dec. 27, 1932, to Resinous Products & Chemical Co.; *Chem. Abs.*, 1933, 27, 1893. see Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., Inc., New York, 1934, 597.

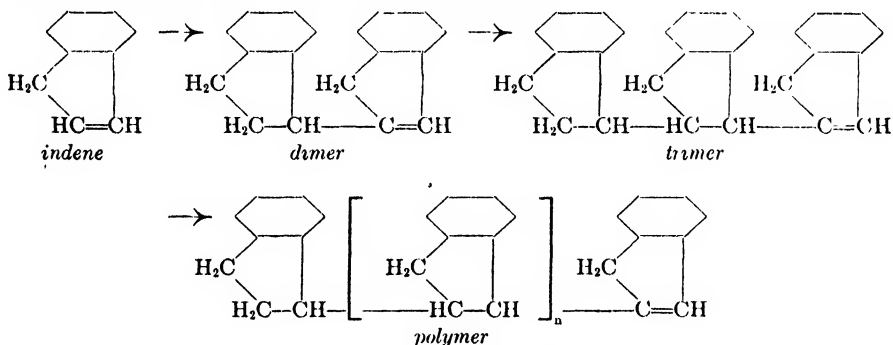
<sup>94</sup> W. Gallay, *Kolloid-Z.*, 1931, 57, 1; *Chem. Abs.*, 1932, 26, 887.

more easily liquefied and less viscous than the higher members. When polyindenes are heated above 300°C., a certain amount of depolymerization occurs and lower polyindenes, diindene and indene itself, are produced in proportions that vary with the conditions.<sup>56</sup>

**Molecular Structure of Polyindene.** Staudinger<sup>57</sup> has put forward this general formula to explain the constitution of polyindenes:



Polymerization mechanism is represented as the formation of long chains connected through the ethylenic linkages. The unsaturated end valences (represented thus, C . . . .), Staudinger considered to be satisfied possibly by the combination of 2 or more such chains into a ring.<sup>57</sup> This explanation of their structure has been criticized by Whitby and Katz<sup>58</sup> on the ground that polyindenes are unsaturated and capable of combining additively with 2 atoms of bromine per molecule. These workers, on the other hand, believe that the polymerization of indene is best represented as proceeding stepwise by the regular addition of successive molecules of monomer to the double bond present at the stage of polymerization immediately preceding, according to the following scheme:



Whitby and Katz consider this explanation of the reaction mechanism to be in accord with the observed facts of thermal polymerization of indene and diindene mixtures and depolymerization of polyindenes, and is not incompatible with the known properties of diindene.

Polymerization of indene is a unimolecular reaction, according to Tammann and Pape,<sup>59</sup> who suggest that the molecules undergo some change before union, the rate of this transformation determining the speed of the entire series of reactions. Increase in pressure is accompanied by an increase in the reaction velocity and a decrease in the initial polymerization temperature.

The constitution and properties of diindene are of importance in explaining the

<sup>56</sup> H. Stobbe and E. Farber, *Ber.*, 1924, 57, 1838. H. Staudinger, H. Johner and V. Wiedersheim, *Helv. Chim. Acta*, 1929, 12, 958. G. S. Whitby and M. Katz, *Can. J. Research*, 1930, 4, 344.  
<sup>57</sup> H. Staudinger, *Ber.*, 1920, 53, 1073. H. Staudinger and J. Fritsch, *Helv. Chim. Acta*, 1922, 5, 787; *J.C.S.*, 1922, 122 (1), 1043.

<sup>58</sup> H. Staudinger, A. A. Ashdown, M. Brunner, H. A. Bruson and S. Wehrli, *Helv. Chim. Acta*, 1929, 12, 984; *Chem. Abs.*, 1930, 24, 612.

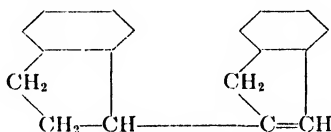
<sup>59</sup> G. S. Whitby and M. Katz, *J.A.C.S.*, 1928, 50, 1162; cf. I. Allen, Jr., V. E. Meharg and J. H. Schmidt, *Ind. Eng. Chem.*, 1934, 26, 663.

<sup>60</sup> G. Tammann and A. Pape, *Z. anorg. allgem. Chem.*, 1931, 200, 113; *Brit. Chem. Abs. A*, 1931, 1239.



general structure of indene polymers. Diindene is a crystalline solid (m.p. 57-58°C.) which readily adds bromine (without the elimination of hydrogen bromide) to yield a dibromide (m.p. 120-121°C.). Diindene can be polymerized by heat or by catalysts, such as sulphuric acid or antimony pentachloride.<sup>100</sup> A mixture of diindene and indene yields trindene on heating. On this account, it is apparent that diindene is an unsaturated hydrocarbon with 1 double bond.

Of the several possible constitutions for diindene, only the structure in which it is represented as 2- $\alpha$ -hydrindylindene, suffices to explain its reactions:



It can be oxidized by chromic acid to yield  $\alpha$ -hydrindene<sup>101</sup> and the ready formation of a monoisitroso derivative with amyl nitrite and sodium ethoxide<sup>102</sup> proves the presence of a reactive methylene group (in the unsaturated five-membered ring system).

The polyindenes can be hydrogenated to hexahdropolyindenes by treatment with hydrogen under high pressure in the presence of a nickel catalyst at 270°C.<sup>103</sup> Complete hydrogenation at this temperature is always accompanied by degradation of more-highly polymerized compounds. The hexahdropolyindenes are white powdery substances, stable towards chemical reagents. Hydrogenation of indene itself under high pressure in the presence of ferric oxide and kieselguhr yields about 80 per cent of resinous polymers.<sup>104</sup>

**Homologues of Indene.** Boes<sup>105</sup> found a mixture of three isomeric methylindenes in the fraction of coal-tar naphtha boiling between 200° and 210°C. The mixture of isomers was at first water-white, but soon turned yellow. Concentrated sulphuric acid resinified the methylindenes, the resulting polymers being free from sulphur and possessing varying degrees of molecular complexity. Hydriodic acid converts methylindenes into resinous polymers. Nitric acid resinifies these hydrocarbons and also partly oxidizes them to a mixture of acids, among which Boes identified hemimellitic and trimellitic acids.

<sup>100</sup> H. Stobbe and E. Farber, *Ber.*, 1924, 57, 1838; G. S. Whitby and M. Katz, *Can. J. Research*, 1930, 4, 344.

<sup>101</sup> H. Stobbe and E. Farber, *Ber.*, 1924, 57, 1838

<sup>102</sup> E. Bergmann and H. Taubadel, *Ber.*, 1933, 65, 463; *Chem. Abs.*, 1932, 26, 2976

<sup>103</sup> H. Staudinger, H. Johnner, G. Schiemann and V. Wiedersheim, *Helv. Chim. Acta*, 1929, 12, 962.

<sup>104</sup> V. N. Ipatiev and N. A. Orlov, *Ber.*, 1929, 62, 593.

<sup>105</sup> J. Boes, *Ber.*, 1902, 35, 1762.

## Chapter 6

### Production of Cumarone Resins

Technical cumarone resins consist principally of mixtures of cumarone and indene polymers, obtained by proper treatment of coal-tar naphtha fractions boiling between 150-200°C. In Chapter 5 the general properties of these substances were described, the discussion presented there indicating that controlled polymerization is necessary to obtain high-quality products. In the commercial production of cumarone resins considerable skill and experience are required. Unless each stage of the process is carefully carried out, sticky, dark-colored materials of limited applicability result. For most purposes cumarone resins should be clean, odorless, pale in color, and possess a melting point of about 135°C. The tars and acid sludges obtained in the usual course of acid-refining of coal-tar naphtha (without special means of separation of the resin contained in them) are not to be confused with cumarone resin, which is a special product.

Experiments on the production of cumarone resin have been described by Ellis and Rabinovitz.<sup>1</sup> A fraction of solvent naphtha boiling between 160-180°C. was treated with 1 per cent of sulphuric acid (sp. gr. 1.84) with good agitation for several hours, the temperature of the mass not rising above 35°C. throughout the operation. The mixture was washed free of acid and distilled with superheated steam to remove naphtha and naphthalene, yielding a residue possessing the consistency of molasses. This soft material was then distilled under 29 inches vacuum up to 180°C. with a loss of 57.5 per cent of its weight. The product was a resin which became plastic at 38°C. and melted completely at 71°C. It had a saponification number of less than 0.2 and an iodine number of 38-43.5. The viscous oily distillate had an iodine number of 28.5. Ellis and Rabinovitz tried a number of other catalysts for the production of resinous polymers, but, with the exception of silver oxide, none was as effective as sulphuric acid. At the boiling point of the naphtha, silver oxide caused the formation of a resin which was harder than that obtained with sulphuric acid. A bright silver mirror formed on the walls of the containing vessel during the reaction.

Some factors involved in the manufacture of technical cumarone resin have been discussed by Marcusson,<sup>2</sup> who stated that such resins can be improved by (1) using only the fraction of solvent naphtha boiling between 160° and 180°C. as raw material, (2) drawing off the sulphuric acid as quickly as possible after polymerization, (3) removing acid resin completely, and (4) separating oily materials from the reaction product by steam distillation under reduced pressure. Marcusson considered that the low melting point of technical resins was due, at least partly, to the indene content of the naphtha, and that higher-melting resins might be obtained by removing indene prior to polymerization. In consequence of this, Kattwinkel<sup>3</sup> attempted to find catalytic agents capable of selectively polymerizing cumarone, but apparently without success. Phosphorus pentoxide

<sup>1</sup> Carleton Ellis and L. Rabinovitz, *Ind. Eng. Chem.*, 1916, 8, 797.

<sup>2</sup> J. Marcusson, *Chem.-Ztg.*, 1919, 43, 93; *Chem. Abs.*, 1919, 13, 2607.

<sup>3</sup> R. Kattwinkel, *Brennstoff-Chem.*, 1924, 5, 5; *Chem. Abs.*, 1924, 18, 2001.

and boric anhydride retarded the polymerization of solvent naphtha by sulphuric acid, possibly owing to the formation of ester-like compounds with the phenols present.

According to Stein,<sup>4</sup> the hardness of cumarone resin is dependent upon the degree of polymerization, and its melting point can be raised by using more concentrated sulphuric acid as polymerizing agent.

In a study of the production of resins from a coal-tar naphtha boiling between 155-185°C., Hirano<sup>5</sup> found that the naphtha should previously be washed with caustic soda solution (sp. gr. 1.22) to remove tar acids, and then with dilute sulphuric acid (sp. gr. 1.20) to remove bases. After drying the naphtha a yield of 9.53 per cent of cumarone resin was obtained by slowly adding 5 cc. of concentrated sulphuric acid to 100 cc. of the well-stirred, purified naphtha. The initial temperature of the oil should be as low as possible and rise in temperature during reaction should be avoided. A paler resin was obtained by thoroughly washing the reaction product with alkali. Other polymerizing agents were also tried. Five cc. of stannic chloride with 100 cc. of naphtha gave 6.06 g. of a hard, pale resin, melting at 85°C.; and 10 g. of aluminum chloride furnished 32.5 g. of a soft, dark resin, melting at 38°C.

German practice for the manufacture of cumarone resins has been described by Glaser.<sup>6</sup> The naphtha was first carefully freed from bases and phenols, and the polymerization then carried out by intimately mixing concentrated sulphuric acid with the naphtha. For this purpose mechanical agitators were employed, since agitation by air resulted in large losses of naphtha. The acid was slowly added in small portions up to a total of about 5 per cent of the charge by weight. During polymerization, a diminution in volume to the extent of 8-12 per cent occurred.

Burda<sup>7</sup> prepared cumarone resins directly from the heavy benzol fraction of coal-tar without the removal of phenols and pyridine compounds. The yield of resin was found to vary with the amount of concentrated sulphuric acid used as polymerizing agent. With less acid, the yield was smaller but the resin was of light color. Repeated treatment of the heavy benzol fraction with 0.5-1 per cent of concentrated sulphuric acid, distilling off volatile hydrocarbons after each addition of acid, yielded at first hard resins, and, later, softer ones. The soft resins could be made harder by heating at 150-180°C. for 20-90 minutes.

The total amount of resin-forming material in solvent naphtha can be determined by adding gradually 2 cc. of concentrated sulphuric acid to 100 cc. of naphtha in a separatory funnel. After running off the acid layer and steam distilling the naphtha, the residue is dehydrated and weighed.<sup>8</sup>

#### COMMERCIAL PRACTICE IN THE PRODUCTION OF CUMARONE RESINS

The commercial production of cumarone resin involves the following distinct steps:

1. Refining the solvent naphtha.
2. Pretreatment of naphtha to remove water and, in some cases, undesirable reactive hydrocarbon constituents.
3. Polymerization.
4. Separation of catalyst (that is, sulphuric acid) and tar sludge.
5. Neutralization of oil.

<sup>4</sup> E. Stein, *Z. angew. Chem.*, 1919, 32, 246; *Chem. Abs.*, 1920, 14, 641.

<sup>5</sup> S. Hirano, *J. Chem. Ind. Japan*, 1922, 25, 827; *Chem. Abs.*, 1923, 17, 3423.

<sup>6</sup> E. Glaser, *Brennstoff-Chem.*, 1921, 2, 99, 113; *J.S.C.I.*, 1921, 40, 519.

<sup>7</sup> I. I. Burda, *Ukrain. Khim. Zhur.*, 1929, 4 (Tech.), 249; *Brit. Chem. Abs. B.* 1930 676.

<sup>8</sup> I. I. Burda, *Ukrain. Khim. Zhur.*, 1929, 4 (Tech.), 257; *Brit. Chem. Abs. B.* 1930, 649.

6. Washing the resin-containing oil.

7. Distillation of oil and recovery of resin as residue.

In the early days of the industry products of low quality were often obtained, but with improved technic and increased attention to details the resin has been greatly improved. The production of cumarone resin in the United States represents a comparatively recent development and the methods adopted reflect to some extent the practice in those countries where the industry was established earlier.

**Refining the Solvent Naphtha.** The solvent naphtha commonly used for the production of cumarone resins is obtained by the fractional distillation of crude coal tar. In older practice, a fraction boiling between 150-200°C. was employed, but the modern tendency is to use narrower cuts, especially those boiling between 160-180°C., since these fractions are rich in cumarone and indene.<sup>9</sup> Polymerization of lower-boiling constituents of coal-tar yields dark resins which are in no way comparable with true cumarone resins. Sometimes the fractionation is regulated so as to furnish a raw material of practically constant cumarone-indene content, or different fractions may be mixed. A raw material containing 30 per cent of resin-forming constituents is stated<sup>10</sup> to be suitable, but fractions having a content of resin-forming substances as high as 80-90 per cent have also been used.<sup>11</sup> In any case the product of the first distillation of coal-tar contains too many impurities and should be very carefully redistilled, preferably in column stills. Only by starting with a sharply fractionated naphtha can high-grade resins be obtained. After careful fractionation, the naphtha is refined to remove phenols, tar acids, naphthalene, and the like. Naphthalene can be removed by freezing and pressing,<sup>12</sup> or by distilling a mixture of the naphtha and a higher-boiling oil (e.g., wash-oil of boiling point 230-330°C.), so that the naphthalene is retained by the residual oil.<sup>13</sup> Phenols are removed by washing with a caustic soda solution, and bases (pyridine and its homologues) by extracting with dilute sulphuric acid. The extraction of bases may be combined with a preliminary polymerization treatment for the removal of dark, resin-forming hydrocarbons by the use of about 5 per cent of sulphuric acid (sp. gr. 1.53).

**Pretreatment and Drying of Naphtha.** A preliminary treatment with sulphuric acid of somewhat lower concentration, or in quantity less than required for the resinification of cumarone and indene, serves to dry the naphtha and also to remove certain readily polymerizable hydrocarbons which yield dark tars.<sup>14</sup> Both objects may be achieved by agitating the naphtha with about 4 per cent by volume of sulphuric acid of 1.53 specific gravity for 45 minutes<sup>15</sup> or by using 0.1-0.5 per cent of more concentrated acid (sp. gr. 1.71-1.84).<sup>16</sup> Under these conditions most of the resins formed separate with the acid sludge and are withdrawn.<sup>17</sup> The naphtha may be neutralized with about 5 per cent by volume of a 15 per cent caustic soda solution, separated from alkali sludge, washed with 20

<sup>9</sup> L. Rabinovitz, U. S. P. 1,416,062, May 16, 1922, to Ellis-Foster Company; *Chem. Abs.*, 1922, 16, 2420. Canadian P. 203,100, 1920; *Chem. Abs.*, 1920, 14, 2994. See also S. Masai, *J. Soc. Chem. Ind. Japan*, 1933, 36, 583B; *Chem. Abs.*, 1934, 28, 916.

<sup>10</sup> C. M. Dennis, U. S. Patent 1,468,440, Sept. 18, 1923, to the Barrett Co.; *Chem. Abs.*, 1924, 18, 175. British Patent 142,806, 1920; *J.S.C.I.*, 1921, 40, 897A. French Patent 514,759, 1920; *Kunststoffe*, 1922, 12, 70. German Patent 400,030, 1920.

<sup>11</sup> R. L. Emery, U. S. P. 1,705,857, Mar. 19, 1929, to Neville Chemical Co.; *Chem. Abs.* 1929, 23, 2310. R. W. Ostermayer, U. S. P. 1,770,281, July 8, 1930, to Neville Chemical Co.; *Chem. Abs.* 1930, 24, 4648.

<sup>12</sup> British P. 156,668, 1921, to Chem. Fabrik Worms A.-G.; *Chem. Abs.*, 1921, 15, 1821.

<sup>13</sup> F. F. Marquard, U. S. P. 1,801,097, April 14, 1931; *Chem. Abs.*, 1931, 25, 3480. Canadian P. 306,628, 1930; *Chem. Abs.*, 1931, 25, 810.

<sup>14</sup> O. Krebs, *Chem.-Ztg.*, 1932, 56, 509; *Brit. Chem. Abs.*, B, 1932, 759.

<sup>15</sup> M. Darrin, U. S. P. 1,297,328, Mar. 18, 1919, to H. Koppers Co.; *Chem. Abs.*, 1919, 13, 1647. British P. 132,229, 1919; *Chem. Abs.*, 1920, 14, 360.

<sup>16</sup> H. C. Karns, U. S. P. 1,541,226, June 9, 1925, to the Koppers Co.; *Chem. Abs.*, 1925, 19, 2277.

<sup>17</sup> Sulphur trioxide has been suggested for removing resins from crude benzene. See W. Gluud, German P. 551,867, 1930, to Ges. für Kohlentechnik m. b. H.; *Chem. Abs.*, 1932, 26, 4944.

per cent of its volume of water and distilled before proceeding to the final polymerizing treatment.<sup>18</sup> In one large-scale method, the wet naphtha is agitated with 0.5 per cent by volume of sulphuric acid (specific gravity 1.71) and the acid, after settling, is drawn off from the dry naphtha. This acid, on account of its dilution by water from the oil, does not cause polymerization of cumarone and indene. Purification by removal of unessential hydrocarbons can also be effected by selective treatment with 2-5 per cent of chlorine, followed by removal of the chlorinated products by distillation.<sup>19</sup>

**Polymerization.** In order to produce hard resins of high melting point and light color, the polymerization of cumarone and indene in solvent-naphtha fractions must be carefully controlled. A dark-colored, soft, sticky resin has comparatively few applications and only light-colored resins are acceptable in varnish making. Hence, the mere production of polymerized material will not suffice unless the product possesses color and hardness comparable with the best natural resins.

In large-scale operations sulphuric acid is employed almost exclusively as the polymerizing agent, for its cheapness and efficiency outweigh any disadvantages connected with its use. However, certain other catalysts will perhaps be used for light-colored, high-melting resins. Such substances as aluminum chloride, ferric chloride, stannic chloride, acid ferric sulphate, and boron trifluoride have been found applicable.

The most important factors to be considered in producing resins by the use of sulphuric acid are (1) the strength and quantity of acid added, (2) the rate of addition of the acid, (3) the degree of admixture of acid with naphtha, (4) the temperature control of the reacting mass, and (5) the duration of the polymerization. The acid must be sufficiently concentrated to yield high-melting resins, but not enough to form dark-colored or sulphonated compounds. The use of too-dilute acid produces soft resins because of extensive low-polymer formation. Owing to the highly exothermic nature of the reaction (said to be caused mainly by the polymerization of indene), slow addition of the polymerizing agent with violent agitation and efficient cooling of the reaction mixture are essential. The process, as usually carried out, consists in running a very slow stream of sulphuric acid of about 93 per cent strength into the solvent naphtha, the mixture being violently stirred by efficient agitators. Thorough means of cooling must also be provided to keep the mixture at about 0°C. during the reaction. The use of an inert diluent also serves to minimize overheating. In any case, the temperature should be kept below 20°C. and may even be lowered to -20°C. A lower temperature of polymerization produces resins of lighter color, and at the same time increases the yield.<sup>20</sup> The concentration and quantity of sulphuric acid used vary somewhat, and probably depend upon the efficacy of mixing, cooling and (more particularly) on the time of reaction. In general practice 0.2-1.0 per cent by volume of 66° Bé sulphuric acid (sp. gr. 1.84) is used,<sup>21</sup> although 1-3 per cent by volume of 62° Bé acid (sp. gr. 1.75) may also be employed at a temperature not exceeding 30-35°.<sup>22</sup> However, by intimately mixing the constituents, employing efficient refrigeration and cutting short the period of reaction, larger quantities of more-concentrated acid may be advantageously employed. The use of 2-5 per cent by volume of 66° Bé sulphuric acid (sp. gr. 1.84) at temperatures between 0°

<sup>18</sup> I. H. Jones, U. S. P. 1,684,868, Sept. 18, 1928, to the Koppers Co.; *Chem. Abs.*, 1928, 22, 4845.

<sup>19</sup> A. O. Jaeger and J. A. Bertsch, U. S. P. 1,853,565, April 12, 1932, to the Selden Co.; *Chem. Abs.*, 1932, 26, 3393.

<sup>20</sup> S. P. Miller, U. S. P. 1,360,665, Nov. 30, 1920, to the Barrett Co.; *Chem. Abs.*, 1921, 15, 605. British P. 160,148, 1920; *Chem. Abs.*, 1921, 15, 2362. Canadian P. 217,322, 1922; *Chem. Abs.*, 1922, 16, 1875. German P. 420,465, 1920.

<sup>21</sup> H. C. Karns, U. S. P. 1,541,266, June 9, 1925, to the Koppers Co.; *Chem. Abs.*, 1925, 19, 2277.

<sup>22</sup> C. M. Dennis, U. S. P. 1,468,440, Sept. 18, 1923, to the Barrett Co.; *Chem. Abs.*, 1924, 18, 175.

and 15° is satisfactory if the reaction is stopped after 10 minutes by the addition of water.<sup>23</sup> The time of reaction can even be reduced to 10 seconds, if the mixture of naphtha and 3 per cent by weight of 66° Bé acid is thoroughly emulsified and cooled.<sup>24</sup>

Typical polymerizing equipment for the treatment of 3000 gallons of dried naphtha (containing 30 to 40 per cent of resin-forming material) consists of a vessel fitted with coils having a cooling surface of 3000 square feet, through which cold brine can be pumped from an insulated tank of 10,000 gallons capacity. The quantity of 66° Bé sulphuric acid used is 90 to 150 gallons for a charge of 3000 gallons of dry naphtha. The oil is first cooled to -10°C. and the acid is added in

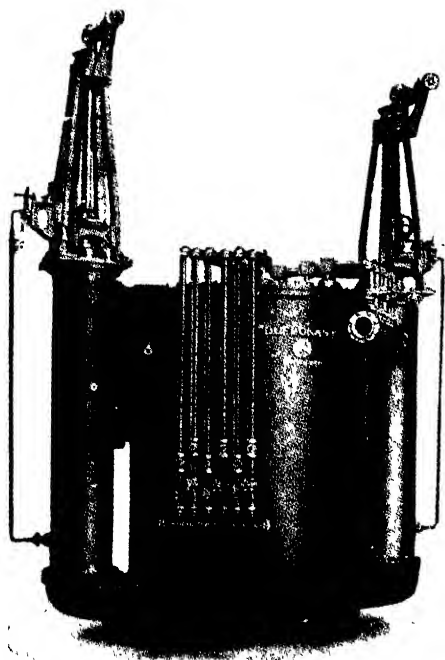


FIG. 44.  
Mixer Applicable in the Production of  
Cumarone Resins

*Courtesy Buffalo Foundry & Machine Co*

2- to 3-gallon portions until 15 gallons have been introduced. The temperature is carefully watched and if it rises above 10°C., the addition of acid is stopped temporarily. The progress of polymerization is watched by determining from time to time the specific gravity of the mix. Since the oil increases in specific gravity during polymerization, the point of no-further-increase will indicate the end of the reaction.

The polymerizing-acid rapidly settles to the bottom of the naphtha, therefore an ordinary paddle agitator is not as satisfactory for mixing as one which constantly elevates the acid from the bottom to the top of the naphtha layer.<sup>25</sup> A rapidly revolving vertical conveyor enclosed by a tube (open at each end) serves to accomplish the mixing. More often, however, mixing is effected by drawing

<sup>23</sup> W. R. Gerges, U. S. P. 1,679,214, July 31, 1928, to the Barrett Co.; *Chem. Abs.*, 1928, 22, 3792

<sup>24</sup> S. P. Miller and J. B. Hill, U. S. P. 1,679,093, July 31, 1928, to the Barrett Co.; *Chem. Abs.*, 1928, 22, 3667.

<sup>25</sup> A mixing apparatus is also described by Miller in U. S. P. 1,670,593, May 22, 1927; *Chem. Abs.*, 1928, 22, 2379.

naphtha and acid from the bottom with a pump and returning the mixture to the top of the polymerizing-vessel. (See Fig. 44.) For the treatment of a 3000-gallon batch of naphtha, a 12-inch pipe running from the bottom to the top of the tank may be used, with the liquid circulated by a centrifugal pump at the rate of 3500 gallons per minute.

**Separation of Acid Tar.** After the polymerizing action has been completed, the oil is allowed to stand so that the heavy tar may settle out. The amount of tar is usually about 2 per cent of the original naphtha, and consists principally of a sludge of acid and sulphonated substances with some entrained naphtha. It is essential that this tar be removed completely and as quickly as possible, otherwise, discoloration of the resin results. At a temperature of 5°C., which seems to be the most satisfactory, 45 minutes are required for the settling of the sludge in a 3000-gallon batch of naphtha. Settling is greatly facilitated, according to Gerges,<sup>26</sup> by dilution of the mixture with 10 volumes of cold water. Under these conditions, separation is complete in 10-15 minutes and the mixture of aqueous acid and sludge suspension can be easily drawn off.

**Neutralization.** When the sludge has been removed, the oil remaining is neutralized with caustic soda solution of specific gravity 1.2-1.8.<sup>27</sup> Use of a weaker solution will cause emulsification and thus prolong the period of settling. The neutralization may be conducted in the polymerization tank or it may be carried out in a cone-shaped settling tank, in which the subsequent washing with water will also take place. If careful separation of acid sludge has been made, the amount of caustic soda solution required will not exceed 1 or 2 per cent of the volume of the batch.

**Washing.** After neutralization is complete, the soda solution is allowed to settle and is drawn off. The neutralized oil is washed free of most of the soluble matter, which consists principally of sodium sulphate and sulphonates and traces of iron salts. Very complete removal of sodium sulphate is necessary since the presence of appreciable amounts of this salt in the resin causes it to whiten on contact with water. The ash content of the resin should be less than 0.3 per cent. For some purposes cumarone resin having an ash content of less than 0.1 per cent is specified.

The washing operation consists of mixing the resin solution with water and agitating by stirrers or compressed air. The settling and separating steps involved in this operation cause a loss of material equivalent to 5-10 per cent of the total naphtha, most of the loss being caused by the formation of emulsions. It has been found that emulsification can be prevented by the use of a 3 per cent aqueous solution of sodium chloride, ammonium chloride, calcium chloride,<sup>28</sup> or hydrochloric acid.<sup>29</sup> About 20 per cent by volume of dilute brine or acid is added to the oil, which is heated to 60-70°C. to facilitate the separation of wash water. Washing may be effected without the use of agitation by introducing water over the oil in the form of a fine spray and allowing it to settle.<sup>30</sup>

**Distillation.** As the final step in the manufacture of cumarone resin, the washed naphtha is distilled off and the resin is obtained as a residue. The distillation is carried out in a steam-jacketed vacuum still equipped with a draw-off and steam-jacketed valve. At the bottom of the still are pipes for the introduction

<sup>26</sup> W. R. Gerges, U. S. P. 1,679,214, July 31, 1928, to the Barrett Co.; *Chem. Abs.*, 1928, 22, 3792.

<sup>27</sup> S. P. Miller, U. S. P. 1,360,665, Nov. 30, 1920, to the Barrett Co.; *Chem. Abs.*, 1921, 15, 605. C. M. Dennis, U. S. P. 1,468,440, Sept. 18, 1923; *Chem. Abs.*, 1924, 18, 175.

<sup>28</sup> S. P. Miller, U. S. P. 1,395,968, Nov. 1, 1921, to the Barrett Co.; *Chem. Abs.*, 1922, 16, 653. British P. 166,818, 1920. *J. S. C. I.*, 1921, 40, 708A. F. H. Rhodes and A. E. Roberts, U. S. P. 1,418,558, Apr. 18, 1922, to the Barrett Co.; *Chem. Abs.*, 1922, 16, 2233.

<sup>29</sup> S. P. Miller and F. H. Rhodes, U. S. P. 1,365,423, Jan. 11, 1921, to the Barrett Co.; *Chem. Abs.*, 1921, 15, 951. British P. 149,962, 1920; *Chem. Abs.*, 1921, 15, 443. German P. 351,296, 1920.

<sup>30</sup> C. M. Dennis, U. S. P. 1,468,440, Sept. 18, 1923, to the Barrett Co.; *Chem. Abs.*, 1924, 18, 175.

of live steam and also a small steam-coil for heating. Naphtha is first withdrawn under a vacuum of about 28 inches. As soon as the flow of distillate begins to drop, live steam is introduced into the bottom of the still and whatever naphthalene is present appears in the receiver first. At this point, the condenser water, which is cold during the distillation of the naphtha, is warmed to about 70-80°C. to prevent choking of the lines. Following the naphthalene, there distils over a heavy oil (boiling at 320-330°C. at atmospheric pressure), which is possibly a by-product of the polymerization of indene. The quantity of this oil depends upon the polymerizing conditions, a greater amount of oily polymers being produced at higher temperatures and with dilute sulphuric acid. Removal of this material is imperative for the manufacture of a high-melting resin and can best be accomplished by steam distillation under high vacuum. However, high-vacuum distillation without the use of steam is preferred by some,<sup>21</sup> because water has a tendency to become emulsified in the resin so that an opaque product results.

According to varnish makers, cumarone resin cannot stand exposure to temperatures above 275°C. without darkening. In this respect it is more sensitive than some of the natural resins. It is not known definitely whether the darkening is due to the thermal instability of the resin itself or to traces of sulphonated substances, but the latter explanation is more likely. From a practical standpoint it is thus important to avoid the use of temperatures exceeding 250-275° during distillation and better results are obtained by operating at lower temperatures (200-250°). This is particularly the case in the production of a varnish resin, where color is of prime importance.

During distillation the melting point of the still-residue is determined from time to time and distillation is continued until the melting point is sufficiently high (usually 135° for a varnish-grade material). The resin is then run into containers at the still temperature. It may be flaked with a chill roll or chipping machine.<sup>22</sup> The distillation of 3000 gallons of polymerized oil may last 60 hours, use of live steam constituting the heaviest item of total manufacturing cost.

To obtain pale elastic cumarone resins it is not only necessary, according to Schneider,<sup>23</sup> to keep the temperature low during the polymerization process, but also during the evaporation of the solvent. High-boiling solvents can be evaporated at comparatively low temperatures by passing a gentle current of air over the material. By keeping the temperature at 90°C. a very pale cumarone resin with a softening point of 80°C. can be made, with an evaporation loss of only 2 per cent of solvent.

#### BY-PRODUCTS OF CUMARONE RESIN MANUFACTURE

A number of by-products are obtained in the manufacture of cumarone resins. The high-boiling oils (b.p. 150-300°C. *in vacuo*) obtained during the distillation of the resin solution are probably low polymers of indene. They have found little industrial application, although Lilienfeld<sup>24</sup> proposed to use them as lubricants, insulating material, transformer oil, for pharmaceutical purposes, or as plasticizers for cellulose ethers. Dennis<sup>25</sup> utilized the by-product oils for the preparation of a cleansing mixture by emulsifying them with soap solution.

A so-called "paracumarone soap" may be produced from the first wash of the

<sup>21</sup> I. H. Jones, U. S. P. 1,684,868, Sept. 18, 1928, to the Koppers Co.; *Chem. Abs.*, 1928, 22, 4845.

<sup>22</sup> S. P. Miller, U. S. P. 1,431,676, Oct. 10, 1922, to the Barrett Co.; *Chem. Abs.*, 1922, 16, 4358.

<sup>23</sup> G. Schneider, *Ber. Ges. Kohlentchnik*, 1921, 39; *Chem. Abs.*, 1922, 16, 3003.

<sup>24</sup> L. Lilienfeld, U. S. Patents 1,625,415 and 1,625,416, April 19, 1927; *Chem. Abs.*, 1927, 21, 2054. British P. 163,271, 1920; *J S C.I.*, 1922, 41, 50A.

<sup>25</sup> C. M. Dennis, U. S. P. 1,365,464, Jan. 11, 1921, to the Barrett Co.; *Chem. Abs.*, 1921, 15, 955.



neutralized solvent naphtha (after polymerization and separation of the acid).<sup>36</sup> By steam-distilling until foaming prevents further treatment, this first wash will yield about 37 per cent of paracumarone soap, 50 per cent of water and 13 per cent of naphtha. A typical paracumarone soap has a total ash content of 10.5 per cent, of which about 6.03 per cent consists of sodium sulphonates. "Sludge paracumarone" is a similar product containing 9.5 per cent of ash (mainly sulphonates).

#### MISCELLANEOUS PROCESSES

A continuous process for the manufacture of cumarone resins has been described by Miller and Hill.<sup>37</sup> Coal-tar naphtha and concentrated sulphuric acid are run separately into a jacketed reaction chamber fitted with a stirrer. The mixture then passes to a settling-tank where separation into two layers takes place. The naphtha, containing dissolved resins, is led into a storage tank and is neutralized and distilled in the usual way. The sulphuric acid is led back into the reaction vessel or to storage. In another continuous process, Miller and Hill subjected

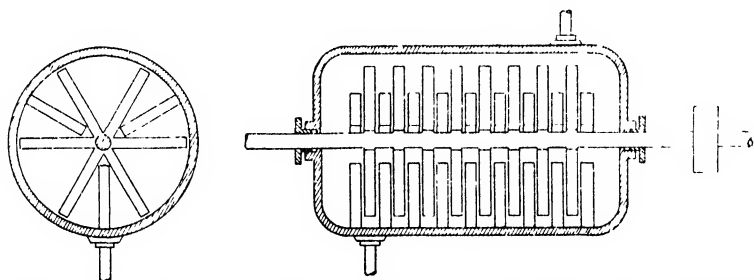


FIG. 45.—Emulsifying Apparatus for the Polymerization of Cumarone. (S. P. Miller and J. B. Hill.)

solvent naphtha to rapid polymerization by emulsifying it with a solution containing a catalyst such as sulphuric acid or aluminum chloride.<sup>38</sup> They stated that the quality of the resin obtained in a continuous-polymerizing process is materially improved if the rate of flow of the reactants through the apparatus is increased. However, at high rates of flow, complete polymerization is conditioned by very intimate contact between the hydrocarbon and the polymerizing agent. By rapidly passing a mixture of naphtha and catalyst between rotating surfaces (spaced 0.005 to 0.10 inch apart and moving relative to one another at a velocity greater than 50 feet per second) very intimate contact is obtained and a time of contact of about 10 seconds is sufficient (see Fig. 45).

In an apparatus described by Miller<sup>39</sup> for the preparation of synthetic resins from solvent naphtha, the required quantity of cooled oil is introduced automatically into a vessel where it is agitated with sulphuric acid, aluminum chloride, or another polymerizing agent. The oil is treated in successive batches, but since all the operations are automatically controlled, the process is in effect continuous. After polymerization, the mixture is withdrawn, spent polymerizing agent and tar are separated, and the oil is neutralized with alkali and distilled.

<sup>36</sup> E. H. Ellms, U. S. P. 1,797,260, Mar. 24, 1931, to the Barrett Co.; *Chem. Abs.*, 1931, 25, 2866.

<sup>37</sup> S. P. Miller and J. B. Hill, U. S. P. 1,464,851, Aug. 14, 1923, to the Barrett Co.; *J.S.C.I.*, 1923, 42, 1081A. Canadian P. 249,081, 1925; *Chem. Abs.*, 1925, 19, 8166.

<sup>38</sup> S. P. Miller and J. B. Hill, U. S. P. 1,679,063, July 31, 1928, to the Barrett Co.; *Chem. Abs.*, 1928, 22, 3667. British P. 225,216, 1923; *Chem. Abs.*, 1925, 19, 1784.

<sup>39</sup> S. P. Miller, U. S. P. 1,752,921, April 1, 1930, to the Barrett Co.; *Chem. Abs.*, 1930, 24, 2594. British P. 246,491, 1926; *Brit. Chem. Abs.*, B, 1927, 722.

Contrary to usual procedure, Roberts<sup>40</sup> proposed to polymerize cumarone and indene in solvent naphtha by use of relatively large proportions of concentrated sulphuric acid for short periods of time, so that at least 10 times as much acid is present as cumarone and indene in the naphtha at any instant. The naphtha is passed continuously through a large volume of concentrated sulphuric acid and the solution of polymerized resin is withdrawn continuously from the top. The acid in the polymerizing chamber is cooled with coils and the heat generated by the polymerization is absorbed completely by the large excess of sulphuric acid. Roberts stated that sufficient sulphuric acid must be present to prevent the heat of reaction from causing a temperature change of more than 30°C. The resins obtained by this polymerization procedure are said to be of lighter color, and to melt about 20°C. higher than those obtained by other processes.

In the process of Wendriner,<sup>41</sup> solvent naphtha is subjected to two successive treatments with sulphuric acid of different concentrations. The naphtha, after being freed from tar acids and bases, is first mixed with 3-5 per cent by volume of 60° Bé sulphuric acid and then 66° Bé sulphuric acid (not more than 0.25 per cent by volume) is continuously added in a thin stream. During the latter step the mixture is agitated vigorously and the temperature allowed to rise to 110-120°C. Stirring is continued until the temperature has fallen to 100° and the mass is allowed to settle. After the acid is removed, the mixture is neutralized and then freed from sodium sulphate. Subsequent distillation with steam produces a clear resin.

Wendriner discovered later, however, that by allowing the temperature to rise secondary reactions took place with the formation of insoluble resins and sulphonated products. By maintaining the temperature at 40-50°C., he not only avoided these reactions but also was able to carry out the polymerization with 66° Bé acid alone. The resin thus produced had a higher melting point and was citron to amber-yellow in color. Wendriner found that if tar acids and bases are not removed prior to polymerization of the cumarone, the resin obtained is not as pure, and more sulphuric acid (0.5 per cent) must be used.

Karns<sup>42</sup> prepared resins which had a lighter color and a greater degree of hardness and transparency than previously obtained, by treating coal-tar distillates, boiling at 140-200°C., with aluminum chloride (0.25 to 1.25 per cent of the weight of oil) at a temperature of about 45°C. The distillate is given a preliminary treatment with a small quantity of sulphuric acid (0.1 to 1.0 per cent of the weight of the oil). The acid is then neutralized and the oil distilled. The treatment with sulphuric acid is insufficient to affect cumarone and indene, but it polymerizes such easily resinified substances as cyclopentadiene, which tend to form dark resins.

In the preparation of very light-colored cumarone resins, Jones<sup>43</sup> employed an initial polymerization to remove unsaturated substances productive of dark resins. The preliminary polymerization is carried out by treatment with about 5 per cent by volume of 50° Bé acid for 45 minutes, after which the sludge and spent acid are separated and the naphtha washed with caustic soda solution, then with water, and finally distilled with steam. The condensate (usually about 90-95 per cent of the original naphtha) is then carefully fractionated, and a cut taken from 150-200°C. is polymerized. The fractionation step is stated to eliminate darkening and softening constituents from the final resin. In an analogous procedure, the addition of ammonium sulphate to the sulphuric acid used in the

<sup>40</sup> A. E. Roberts, U. S. P. 1,515,315, Nov. 11, 1924, to the Barrett Co.; *Chem. Abs.*, 1925, 19, 186.

<sup>41</sup> M. Wendriner, German P. 270,993, 1912; *J.S.C.I.*, 1914, 33, 474; *Chem. Abs.*, 1914, 8, 2248.

German P. 281,432, 1913; *Chem. Abs.*, 1913, 9, 2001.

<sup>42</sup> H. C. Karns, U. S. P. 1,541,226, June 9, 1925, to the Koppers Co.; *Chem. Abs.*, 1925, 19, 2277.

<sup>43</sup> I. H. Jones, U. S. P. 1,684,868, Sept. 18, 1928, to the Koppers Co.; *Chem. Abs.*, 1928, 22, 4845.

second polymerization is said to be of value in obtaining light-colored products. It is also stated that practically colorless resins result if a mixture of 15 parts of sulphuric acid, 4 parts of acetic acid and 1 part of water is used as polymerizing-catalyst.<sup>44</sup>

Cline obtained light-colored cumarone resins from oils which ordinarily yield dark resins.<sup>45</sup> The essential feature of his procedure is a preliminary treatment of crude coal-tar naphtha by refluxing it for an hour with 5 per cent of litharge. This treated oil is then removed by decantation and subsequently vacuum-distilled in contact with an alkaline material. The distillate coming over at temperatures up to 200°C. (at atmospheric pressure) is polymerized with sulphuric acid (sp. gr. 1.83) in the presence of refined naphtha as a diluent. This method recovers 80-85 per cent of the total polymerizable constituents as resin.

In the process of Rabinovitz,<sup>46</sup> solvent naphtha (b. p. 160-180°C.) is treated with a slow stream of sulphuric acid (sp. gr. 1.84) under good agitation. The acid is withdrawn and the naphtha washed with a 5 per cent alkali solution. The solvent naphtha is then distilled with superheated steam and the viscous residue is hardened by distillation under a vacuum of 29 inches until the temperature reaches 180°C. The resulting pale, hard resin has an iodine number of 47.

Meyer<sup>47</sup> prepared a light-colored resin of high softening point by polymerizing cumarone and indene with acid in the usual manner and then neutralizing the acid present by vigorously agitating it with a slight excess of powdered alkali or alkaline-earth carbonates, preferably with the addition of a small quantity of barium or sodium peroxide. The neutral liquid was then separated by decantation, filtration, or centrifuging and the volatile constituents removed by distillation.<sup>48</sup>

Anhydrous metallic chlorides, such as aluminum chloride or ferric chloride, were used by Demant<sup>49</sup> for the polymerization of the unsaturated compounds in crude benzene to yield resinous products which soften above 100°C. After removal of the catalyst by washing with water, the resins are obtained by distilling off the benzene. They can be used for varnishes without further purification.<sup>50</sup> The polymerization is effected without external heating and, if necessary, with cooling. Hydrated metallic chlorides can be used to produce high-melting cumarone resins. Stirring coal-tar distillates with small quantities of hydrated aluminum or ferric chlorides causes polymerization without external heating.<sup>51</sup> Supan<sup>52</sup> employed ferric chloride for the production (from crude benzene fractions) of resins having a softening point as high as 170°C. For example, 2 per cent of crystalline ferric chloride is added gradually to a crude benzene fraction (b. p. 160-180°C.) heated to 50°C., and the mixture is cooled to prevent too great a rise in temperature. On completion of the reaction, the liquid is washed with water and sodium carbonate solution, and the resin is separated by distilling off the unchanged liquid. Oil-soluble metallic chlorides, e.g., titanous chloride, have also been suggested as catalysts.<sup>53</sup>

In order to control the degree of polymerization of cumarone, Copthorne and

<sup>44</sup> J. Bojanovski, B. Gizinski and T. Rabek, *Przemysl Chem.*, 1934, 18, 321; *Brit. Chem. Abs. B*, 1935, 161.

<sup>45</sup> E. L. Cline, U. S. P. 1,942,201, Jan. 2, 1934, to the Barrett Co.; *Chem. Abs.*, 1934, 28, 1881.

<sup>46</sup> L. Rabinovitz, U. S. P. 1,418,062, May 16, 1922, to Ellis-Foster Co.; *Chem. Abs.*, 1922, 16, 2420. Canadian P. 203,100, 1920; *Chem. Abs.*, 1920, 14, 2994. Cf. Carleton Ellis and N. L. Foster, *British P.* 117,016, 1917, to Ellis-Foster Co.; *Chem. Abs.*, 1918, 12, 2451.

<sup>47</sup> F. H. Meyer, *German P.* 294,107, 1916; *J.S.C.I.*, 1916, 35, 1164.

<sup>48</sup> See also G. S. Walpole, *British P.* 145,415, 1920; *Chem. Abs.*, 1920, 14, 3163.

<sup>49</sup> J. Demant, *German P.* 392,090, 1917; *J.S.C.I.*, 1925, 44, 16B.

<sup>50</sup> Employing the chlorides of aluminum and iron instead of sulphuric acid in the polymerization improves the mechanical strength and thermal resistance of cumarone resins, according to M. Mikhailov and M. Stolyarov, *Plast. Masses*, 1933, (5), 12; *Chem. Abs.*, 1934, 28, 8000.

<sup>51</sup> *German P.* 446,707, 1918, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1928, 762.

<sup>52</sup> A. Supan, *German P.* 394,217, 1923, to Oberschlesische Kokswerke A.-G.; *J.S.C.I.*, 1925, 44, 16B.

<sup>53</sup> French P. 607,672, 1925, to Comp. des mines de Vicoigne Neoux et Drocourt; *Brit. Chem. Abs. B*, 1927, 211. French P. 688,542, 1929; *Chem. Abs.*, 1931, 25, 802.

Tannehill<sup>64</sup> proposed the dilution of tar- and base-free solvent naphtha (b. p., 150-200°C.) with lighter naphthas (b. p., 130-150°). Another suggestion made by Tannehill was neutralization of the acid by ammonia gas to arrest polymerization while the resin is still in a highly fluid state.

A dilution method was also used by Emery.<sup>65</sup> A distillate containing as high as 80 per cent of cumarone and indene, prepared by fractional distillation, is polymerized and then diluted with petroleum benzine in order to facilitate removal of insoluble substances. The resin solution is then decanted, washed free of acid and distilled under high vacuum, live steam being used to remove heavy oils. Ostermayer<sup>66</sup> employed a similar cut rich in cumarone and indene as initial material, but diluted the polymerized material with petroleum distillates both higher and lower in specific gravity than petroleum benzine. The product obtained, when using petroleum distillate of low specific gravity, is of slightly lower melting point and not so clear as when heavier petroleum distillates (kerosene or wash oils) are employed; but the procedure is facilitated in the former case. Ostermayer stated that better control of the process is obtained by diluting the naphtha with petroleum distillates, either before or during the polymerization. However, the products are darker and of lower melting point than when dilution is effected after polymerization.

A clear, transparent resin of high melting point for use in varnishes is obtained by carrying out the polymerization in a mixture containing a relatively small quantity of crude solvent naphtha in proportion to the diluent (a coal distillate or petroleum distillate). Dilution serves to prevent rise in temperature. After the initial polymerization, additional small quantities of crude naphtha and catalyst are run into the batch until a final concentration of 25 per cent of polymers exists. Up to this point only 3-5 per cent of sulphuric acid (sp. gr. 1.83) is needed. Recovery of resin from here proceeds in the usual manner.<sup>67</sup> An improvement in this method consists in dispersing the sulphuric acid catalyst in the diluent and then adding the solvent naphtha at a controlled rate.<sup>68</sup>

Crude benzene was used by Schneider and Nettlebusch<sup>69</sup> to produce resins by the dilution method. The benzol was diluted with solvent naphtha or with an oil boiling at 200-230°C., and then mixed with sulphuric acid (80-93 per cent) at 10-40°C. Distillation yielded motor fuel, oil and resin.

A process of Jaeger and Bertsch<sup>70</sup> includes treatment of the naphtha with chlorine prior to polymerization. After phenols and bases have been removed and the naphtha has been partially purified by washing with a small amount of sulphuric acid, chlorine is introduced. Chlorine reacts with the unsaturated and saturated aliphatic and alicyclic compounds (including hydrindene, cyclopentadiene, dicyclopentadiene, styrene) as well as with sulphur compounds such as thioxene, and transforms them into high-boiling chloro derivatives, but cumarone and indene are practically unattacked. For example, a solvent naphtha boiling at 150-180°C. is treated with 1-3 per cent of chlorine, or with an equivalent amount of bromine.

<sup>64</sup> H. N. Copthorne and A. L. Tannehill, U. S. P. 1,353,220, Sept. 7, 1920; *Chem. Abs.*, 1920, 14, 3807. A. L. Tannehill, U. S. P. 1,389,791, Sept. 6, 1921; *Chem. Abs.*, 1922, 16, 167.

<sup>65</sup> R. L. Emery, U. S. P. 1,705,857, Mar. 19, 1929, to Neville Chemical Co.; *Chem. Abs.*, 1929, 23, 2310.

<sup>66</sup> R. W. Ostermayer, U. S. P. 1,770,261, 1,770,282 and 1,770,283, July 8, 1930, to Neville Chemical Co.; *Chem. Abs.*, 1930, 24, 4643.

<sup>67</sup> G. K. Anderson, U. S. P. 1,922,342, Aug. 15, 1933, to Neville Chemical Co.; *Chem. Abs.*, 1933, 27, 5203.

<sup>68</sup> G. K. Anderson, U. S. P. 1,990,215, Feb. 5, 1935, to the Neville Company; *Chem. Abs.*, 1935, 29, 1903.

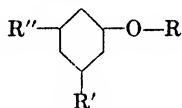
<sup>69</sup> R. Schneider and L. Nettlebusch, British P. 280,495, 1931, to Concordia Bergbau A.-G.; *Brit. Chem. Abs.*, B, 1932, 1018. French P. 718,436, 1931; *Chem. Abs.*, 1932, 26, 3094.

<sup>70</sup> A. O. Jaeger and J. A. Bertsch, U. S. P. 1,853,565, April 12, 1932, to the Selden Co.; *Chem. Abs.*, 1932, 26, 3898. A. O. Jaeger, U. S. P. 1,741,305, Dec. 31, 1929, to the Selden Co.; *Brit. Chem. Abs. B*, 1930, 940.

The chlorine or bromine is introduced in gaseous form mixed with an inert gas, and a small amount of calcium carbonate is added to neutralize acidity. After chlorination, the solvent naphtha is distilled off from the higher-boiling chlorinated substances and is polymerized either under heat and pressure or by addition of concentrated sulphuric acid at temperatures below 25°C. The product is neutralized, washed with water and distilled *in vacuo*. After superheated steam has been blown through the still-residue, an almost colorless resin is obtained.

Hofmann and Stegemann<sup>61</sup> obtained cumarone resin by shaking cumarone oil for some hours at ordinary temperature with hydrogen fluoride, boron trifluoride, or with a mixture of hydrogen fluoride and an inorganic halide. The hydrogen fluoride can be expelled from the product by heat.

Modified cumarone resins, soluble in all proportions in commercial benzenes (even at ordinary temperatures) and also in drying oils, have been prepared by Rosenthal by polymerizing solvent naphthas (freed from phenols and bases) with catalysts such as stannic chloride, zinc chloride, concentrated sulphuric acid, ferric chloride, fluoboroacetic acid and antimony pentachloride, in the presence of meta-substituted aryl alkyl ethers of the general formula:



in which R and R' stand for alkyl groups and R'' represents hydrogen or an alkyl group.<sup>62</sup> Because of their solubility and stability to light, the modified resins have been suggested for the manufacture of oil varnishes. The properties of these resins vary with the catalyst employed. Fluoboroacetic acid yields nearly-colorless, high-melting resins soluble in drying oils. Lower-melting resins, light brown in color and also oil-soluble, are produced under the influence of sulphuric acid. The use of stannic chloride as a catalyst leads to the formation of very light-colored resins, insoluble in stand oils but soluble in ordinary drying oils. In one preparation, 1000 parts by weight of solvent naphtha (boiling point 163-182°C., containing 52 per cent of cumarone and indene and free from phenols and bases) are mixed with 86 parts of m-xylyl ethyl ether, and the mixture, heated to 40°, is treated with 10 parts by weight of fluoboroacetic acid. When the reaction is complete, the mass is diluted with 200 parts of xylene or purified solvent naphtha and treated, while hot, with 60 parts of calcium oxide or barium oxide. The resin solution is filtered from the precipitate and the volatile constituents are distilled off completely *in vacuo*. There are obtained 545 parts of a nearly colorless resin melting at 133° and readily soluble in cyclohexane, aliphatic and hydroaromatic hydrocarbons, linseed oil, tung oil, and stand oil.

In the polymerization of cumarone and indene in solvent naphthas, Weiss recommended the use of a special solid catalyst consisting of an acid ferric sulphate mixed with an absorbent such as fuller's earth.<sup>63</sup> Some advantages noted in the use of this polymerizing-catalyst are that the reaction is very gradual, with no tendency to superheating; the removal of polymerizing agent together with the tarry matter is quickly accomplished by filtration (in contradistinction to the long

<sup>61</sup> F. Hofmann and W. Stegemann, German P. 492,345, 1928; *Chem. Abs.*, 1930, 24, 2905.

<sup>62</sup> L. Rosenthal, U. S. P. 1,860,479, May 31, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4191. German P. 497,413, 1928; *Chem. Abs.*, 1930, 24, 3663. French P. 677,512, 1929; *Chem. Abs.*, 1930, 24, 3123. British P. 314,810, 1929; *Chem. Abs.*, 1930, 24, 1530.

<sup>63</sup> J. M. Weiss, U. S. P. 1,894,934, Jan. 17, 1933; *Chem. Abs.*, 1933, 27, 2592. British P. 338,845, 1929; *Chem. Abs.*, 1931, 25, 2581. French P. 698,623, 1930; *Chem. Abs.*, 1931, 25, 3185. German P. 575,919, 1933; *Chem. Abs.*, 1933, 27, 5996.

period of settling required when sulphuric acid is used); and the absorption of dark-colored by-products by the porous carrier gives a light-colored product. The catalyst is prepared by thoroughly incorporating concentrated sulphuric acid (proportionately in excess of that necessary to form ferric sulphate) in a mixture of ferric oxide and absorbent earth, drying the mass, and powdering it to a size of about 20- to 30-mesh. Crude solvent naphtha (1 gallon), having a boiling range of 160-190°C., is vigorously agitated with about 0.5 pound of this catalyst for two hours at 55°C. or higher, after which the mass is filtered. The filtered solution is washed, first with a dilute alkaline solution and then with water. The resins are recovered by distillation under reduced pressure with superheated steam. The naphtha may be given an acid wash with sulphuric acid (sp. gr. 1.53) prior to the polymerizing treatment.

Cumarone resins of uniform properties, having melting points up to 135°C., were prepared by Sperr and Darrin<sup>64</sup> by polymerizing crude solvent naphtha under the influence of heat and pressure. The naphtha is heated to 100-450° under pressures ranging from 50-300 pounds per square inch for periods of from 1-10 hours, after which the volatile constituents are distilled off, the end-temperatures of the vapors being 150-300°C. The resulting mass is then blown with air or steam to remove high-boiling oils and the resin is drawn off. The rate of resinification is increased and the hardness of the resins improved by the use of catalysts consisting of strips of copper, silver, gold, or platinum immersed in the liquid.<sup>65</sup> The resins thus obtained are said to be harder than those from acid processes, and can be ground easily without sticking or gumming.<sup>66</sup> They possess a clear, reddish color and are useful for electrical insulation or for varnish making.

Cumarone resin produced by polymerization with sulphuric acid often retains acid substances. Ellis<sup>67</sup> removed these substances by fusing the resin with basic neutralizing agents in the absence of sufficient water to dissolve the basic material. The neutralized resins are then useful for the manufacture of concrete-floor varnishes and other coatings where a neutral resin is required.

The purification of crude cumarone resin was accomplished by Singer,<sup>68</sup> by washing with solvents (e.g., alcohol, acetone, or chlorinated hydrocarbons) to remove oily materials.

### MODIFIED CUMARONE RESINS

Modified cumarone resins are produced by adding to the solvent naphtha substances which alter the nature of the resin obtained. For instance, the condensation of solvent naphtha (b. p., 160-190°C.) to which phenols have been added, yields materials with disinfectant or therapeutic properties, and which are also useful for making lakes and dyes. For this treatment catalysts which have been employed include halogen acids, metallic chlorides<sup>69</sup> and acid salts.<sup>70</sup> A modified resin has also been produced by using the phenols already present in the solvent

<sup>64</sup> F. W. Sperr, Jr. and M. Darrin, U. S. P. 1,263,813, Apr. 23, 1918, to the Koppers Co., *Chem. Abs.*, 1918, 12, 1704. U. S. P. 1,296,776, Mar. 11, 1919. *J. S. C. I.*, 1919, 38, 379A. Canadian P. 184,890, 1918. *Chem. Abs.*, 1919, 13, 196. British P. 123,806, 1918; *J. S. C. I.*, 1919, 38, 263A.

<sup>65</sup> An apparatus for carrying out this process was described by Sperr and Darrin in U. S. P. 1,314,613, Sept. 2, 1919; *Chem. Abs.*, 1919, 13, 2619.

<sup>66</sup> M. Darrin, U. S. P. 1,326,579, Dec. 30, 1919, to the Koppers Co.; *Chem. Abs.*, 1920, 14, 643.

<sup>67</sup> Carleton Ellis, U. S. P. 1,570,584, Jan. 19, 1926, to Ellis-Foster Co.; *Chem. Abs.*, 1926, 20, 832.

<sup>68</sup> L. Singer, British P. 109,270, 1917; *Chem. Abs.*, 1918, 12, 93. Norwegian P. 29,034, 1918, *Chem. Abs.*, 1919, 13, 905.

<sup>69</sup> J. Rosenthal and W. Kropp, German P. 499,825, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 4524. British P. 297,075, 1927; *Chem. Abs.*, 1929, 23, 2539. French P. 636,606, 1927; *Chem. Abs.*, 1929, 23, 607.

<sup>70</sup> E. Tschunkur and F. Eichler, German P. 535,078, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3393. British P. 349,934, 1930; *Brit. Chem. Abs. B.*, 1931, 918. French P. 39,642, 1931, addn. to 636,606; *Chem. Abs.*, 1932, 26, 4827.

naphtha.<sup>71</sup> It was found that the presence of phenols rendered the resin alcohol-soluble and therefore useful for lacquer preparations.

Very light-colored resins were prepared by Rosenthal by polymerizing solvent naphthas in the presence of phenols and under the catalytic influence of double compounds of boron trifluoride and carboxylic (or hydroxycarboxylic) acids.<sup>72</sup> When the reaction mixture contains phenols to the extent of 9 per cent or more of the quantity of indene present in the solvent naphtha, resins soluble in stand oil (prepared by heating linseed oil) are formed. The reaction is carried out by slowly adding small quantities (usually 1-5 per cent) of the fluoboro-fatty acids to the mixture of crude solvent naphtha and phenols at a temperature of about 60°C. For example, a resin soluble in linseed oil is prepared by allowing 2 parts of fluoboroacetic acid to run slowly for 2-3 hours into 100 parts of crude solvent naphtha (b. p., 155-192°C.), containing 58 per cent of cumarone and indene and 4 per cent of phenolic constituents. The temperature increases to about 60°C. (initial temperature is 35°) and stirring is continued for 6 or 7 hours. The mixture is then heated to 80-90°C. for one-half hour with the addition of 25 parts of xylene and 6-8 parts of barium oxide. The volatile constituents of the filtered reaction-liquid are then distilled *in vacuo* to furnish 55 parts by weight of an almost colorless resin which sinters at 140° and melts at 160°. By treating a mixture of 600 parts of solvent naphtha having a cumarone content of 20 per cent and an indene content of 36 per cent, and 21 parts of crude cresol (or 33 parts of  $\beta$ -naphthol) with fluoboroacetic acid as above, 320 parts of a very light-colored resin, melting at 147° and soluble in linseed oil, are obtained.

Rosenthal<sup>73</sup> also prepared light-colored, oil-soluble resins by condensing solvent naphtha containing cumarone and indene, with at least 10 per cent of phenols (calculated on the amount of resinifiable constituents present) with anhydrous or crystallized ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) as catalyst. The melting points of the resins depend upon the relative proportions of phenol and indene present. The following example concerns the treatment of a mixture of 200 parts (by weight) of a phenol- and base-free naphtha, boiling at 160-186°C. and containing 46.8 per cent of indene and 15.2 per cent of cumarone. Nine parts of phenol are introduced and then 14 parts of molten ferric chloride, at an initial temperature of 20°C. As reaction proceeds the temperature rises to 52-55°C. Stirring is continued for 6-8 hours and the temperature is maintained below 60°C. The mass is then diluted with 100 parts of xylene to remove iron compounds, and stirred with 10 parts of quicklime. The solvent is removed from the filtered resin solution by vacuum distillation, and a light resin is obtained which sinters at 125°C. and melts at 158°C.

Cumarone resin can be modified so as to increase its melting point by treating it with concentrated sulphuric acid in the presence of a solvent.<sup>74</sup> The solution is then neutralized with alkaline earths and the solvent removed by evaporation.

According to Staudinger,<sup>75</sup> hydrogenation of parindene resins renders them more resistant to heat and chemical action. Hydrogenation may be carried out under 50 to 70 atmospheres pressure and at about 270° employing a metal of Group 8 as catalyst.

<sup>71</sup> German P. 302,543, 1917 to Rütgerswerke-A.-G.; *J.S.C.I.*, 1920, 39, 307A.

<sup>72</sup> L. Rosenthal, U. S. P. 1,857,333, May 10, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4191. British P. 310,816, 1929; *Chem. Abs.*, 1930, 24, 740. French P. 674,240, 1929; *Chem. Abs.*, 1930, 24, 2624. German P. 517,477, 1928 and 520,858, 1929; *Chem. Abs.*, 1931, 25, 2313, 3186.

<sup>73</sup> L. Rosenthal, U. S. P. 1,863,814 and 1,863,831, June 21, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4488. German P. 548,436, 1926; *Chem. Abs.*, 1932, 26, 3687. British P. 306,501, 1927; *Brit. Chem. Abs. B.*, 1929, 366. French P. 644,015, 1927; *Chem. Abs.*, 1929, 23, 1764.

<sup>74</sup> German P. 325,875, 1918; to Rütgerswerke-A.-G.; *J.S.C.I.*, 1921, 40, 19A.

<sup>75</sup> H. Staudinger, German P. 504,215, 1926; *Chem. Abs.*, 1930, 24, 5518. For the hydrogenation of cumarone resin see British P. 247,586, 1925; to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1927, 21, 643. See also H. Winter and G. Free, *Brennstoff-Chem.*, 1934, 15, 267; *Brit. Chem. Abs. B.*, 1934, 914.

Kessler<sup>76</sup> found that a coal-tar fraction (boiling at 150-250°C.), treated with an excess of formaldehyde<sup>77</sup> or other aldehyde in the presence of a trace of ammonia or caustic soda at 150°C., produced oils which dried on exposure to the air and slowly polymerized at this temperature. According to Hönel,<sup>78</sup> low-melting cumarone resins were rendered harder and higher-melting by heating them with 20 per cent of the condensation product of formaldehyde and p-amyphenol at 200°. A cumarone resin can be made less brittle by adding to it 5 to 10 per cent of drying oils, fats or waxes.<sup>79</sup>

Jaeger<sup>80</sup> recommended a phthalide or hydrogenated phthalide as a plasticizer for cumarone resin. About 12 per cent of phthalide is added to the fused resin, or the phthalide can be mixed with a solution of the resin to form a lacquer which dries to a flexible film.

Resinous products similar to cumarone resins have been obtained from naphtha fractions of higher boiling point than those ordinarily used. For instance a fraction boiling at 190°-240°C. has been utilized.<sup>81</sup>

Likewise light benzene fractions yield homologous resins. Demant<sup>82</sup> heated such fractions with sulphuric or phosphoric acid and obtained viscous oils which on further treatment could be used in varnish making. Krieger<sup>83</sup> treated a benzol fraction (80°-160°C.) with sulphuric acid, washed the product with water and alkali, and then distilled it in the presence of caustic soda. The still-residue yielded a brown, almost ash-free liquid (b. p., 260-360°C.), suggested as a lubricant.

The process of Damm for the purification of benzenoid oils yields resinous materials as by-products.<sup>84</sup> The oil is agitated with sulphuric acid (sp. gr. 1.71-1.83) and allowed to settle into 3 layers: acid, acid resin, and oil. After withdrawal of the acid, the remaining layers are neutralized with dilute caustic soda. The original impurities are thus liberated from the acid-resin layer in modified form and dissolved in the oil phase. The oil layer is then removed and the resin recovered from the acid-resin portion.

#### RESINS FROM ACID TAR

Strictly speaking, acid resins obtained from the sulphuric acid used in washing coal-tar light oils are not cumarone resins, but, since they are related, brief mention may be made of these products. The acid resins are usually obtained by adding water to the sulphuric acid used in refining coal-tar oils and then heating the solution without carbonizing the resins present. The dilute acid solution is extracted with a hydrocarbon such as benzol, and the resin, separated by evaporation of the solvent, may be utilized by adding it to solutions of other resins. By the above procedure, Hilpert<sup>85</sup> obtained a resin in the form of a bright yellow powder useful as a base for a quick-drying lacquer. The resin from the acid used to refine naphthalene is dark brown in color. Thorp and Thorp<sup>86</sup> recovered such resins in the following manner: The waste tar acid is agitated with from 1/2 to 1 volume

<sup>76</sup> J. J. Kessler, U. S. P. 1,616,321, Feb. 1, 1927; *Chem. Abs.*, 1927, 21, 1003.

<sup>77</sup> For indene-formaldehyde resins see Chapter 12.

<sup>78</sup> H. Hönel, U. S. P. 1,800,925, Apr. 14, 1931, to Beck, Koller & Co.; *Chem. Abs.*, 1931, 25, 3503. Austrian P. 120,679, 1930; *Chem. Abs.*, 1931, 25, 2012. German P. 563,876, 1928; *Chem. Abs.*, 1933, 27, 1220.

<sup>79</sup> German P. 348,088, 1919, to Chem. Fabr. Worms. A.-G.; *J.S.C.I.*, 1922, 41, 382A.

<sup>80</sup> A. O. Jaeger, U. S. P. 1,892,769, Jan. 3, 1933, to the Selden Co.; *Chem. Abs.*, 1933, 27, 2319.

<sup>81</sup> British P. 156,668, 1921; to Chem. Fabrik. Worms. A.-G.; *Chem. Abs.*, 1921, 15, 1821.

<sup>82</sup> J. Demant, British P. 179,610, 1921; *Chem. Abs.*, 1922, 16, 3387.

<sup>83</sup> A. Krieger, German P. 383,291, 1921; *J.S.C.I.*, 1923, 42, 262A.

<sup>84</sup> P. Damm, U. S. P. 1,817,804, Aug. 4, 1931, to the Koppers Co.; *Brit. Chem. Abs.*, B, 1932, 459.

<sup>85</sup> S. Hilpert, U. S. P. 1,427,386, Aug. 29, 1922, to Deutsch-Luxemburg. Bergw. & Hutten. A.-G.; *J.S.C.I.*, 1922, 41, 803A. German P. 319,010, 319,011, 320,808 and 324,722, 1916; *J.S.C.I.*, 1920, 39, 577A, 665A, 792A. German P. 341,698, 1917; *J.S.C.I.*, 1922, 41, 23A. British P. 157,715, 1921; *J.S.C.I.*, 1922, 41, 355A.

<sup>86</sup> F. Thorp and H. T. Thorp, British P. 124,605, 1918; *J.S.C.I.*, 1919, 38, 318A.



of water. On standing, a pasty mass of tar oil and resin settles out. This mass is washed with water and steam distilled. The resinous residue of the steam distillation is washed with alkali and dried. Schümmer<sup>87</sup> distilled the residue, obtained in a similar way, under reduced pressure and recovered the sulphur dioxide for conversion into sulphuric acid. Another method involves running the acid tars into boiling water.<sup>88</sup> The floating resin-layer is then drawn off and worked into a hard resin by treatment with steam, ammonia or alkali.

Kugel and Schwenke<sup>89</sup> neutralized the wash-acid from the refining of benzol with ammonia and diluted the precipitated resinous substances with benzol or solvent naphtha while agitating and cooling the liquid. After separation from the ammonium sulphate, the solvent is distilled from the resins.

In order to remove the resinous sludge from the sulphuric acid used for washing benzol, Still<sup>90</sup> heated the acid in a receptacle in the lower part of which a removable perforated tray is placed. After all the treated acid has been discharged from the still, the whole of the solid resin is lifted out on the tray. As a substitute for sulphuric acid in effecting removal of tar- and gum-forming impurities from benzene, the use of a slightly acidic potassium permanganate solution has been suggested.<sup>91</sup> This treatment causes the oxidation and polymerization of all olefinic substances in the benzene.

The still-residues from the redistillation of acid-treated and neutralized crude benzols (also carburetted water-gas tar, or "holder oil" and Pintsch gas "hydrocarbon drips") are high-boiling viscous sulphurous oils, which on prolonged heating are converted into pitch or resin.<sup>92</sup> This has been erroneously designated "cumarone resin" by some manufacturers. It is probable that the residues are derived from diolefinic compounds present in the original crude benzols.

Kattwinkel considers that sulphur present in the acid resin is in the form of neutral saturated sulpho-acid esters.<sup>93</sup> Upon removing the acid from such an acid resin and drying at 100°C., he obtained a dark violet-colored resin which could be easily pulverized. He extracted with aniline the powdered resin thus obtained and distilled the extract *in vacuo*. Removal of excess aniline by heating on a water bath left a pitch residue recommended for roofing compositions or for binders in coal or lignite briquettes.<sup>94</sup>

Sulphonated cumarone resins have been used to a small extent in various ways, such as in leather tanning,<sup>95</sup> in the production of viscose fibers<sup>96</sup> and in the form of their copper salts in mixtures for combating plant diseases.<sup>97</sup>

Benzol-still residues were used by Wagner in preparing cutting oils and gear-shield oils.<sup>98</sup> The residue is mixed with petroleum and water, heated to 80°C. and then allowed to cool and settle. The oily top layer is decanted, and the semi-solid material remaining is heated to 200°, whereupon the oily layer previously removed is again added to produce the cutting oil.

<sup>87</sup> J. Schümmer, German P. 320,255, 1918; *J.S.C.I.*, 1920, 39, 633A.

<sup>88</sup> G. W. J. Bradley, British P. 412,343, 1934, to Woodall-Duckham, Ltd.; *Brit. Chem. Abs. B*, 1934, 822.

<sup>89</sup> E. Kugel and H. Schwenke, German P. 454,307, 1922, to Zeche de Wendel; *Brit. Chem. Abs.*, B, 1929, 588.

<sup>90</sup> C. Still, British P. 219,089, 1923 and 277,619, 1926, to Coke & Gas Ovens, Ltd.; *Chem. Abs.*, 1925, 19, 582; 1928, 22, 2656.

<sup>91</sup> O. Guillet, French P. 761,454, 1934, to Soc. anon. "Compagnies reunies du gaz et d'électricité"; *Chem. Abs.*, 1934, 28, 4073.

<sup>92</sup> B. T. Brooks and I. Humphrey, *J.A.C.S.*, 1918, 40, 853. R. Weissgerber, *Ber.*, 1928, 61, 2111; *Chem. Abs.*, 1929, 23, 501.

<sup>93</sup> R. Kattwinkel, *Brennstoff-Chem.*, 1923, 4, 55, 377; *Chem. Abs.*, 1923, 17, 2487.

<sup>94</sup> R. Kattwinkel, German P. 395,597, 1923; *J.S.C.I.*, 1925, 44, 4B.

<sup>95</sup> R. B. Croad, *J.S.C.I.*, 1923, 42, 177.

<sup>96</sup> French P. 612,879, 1926, to Köln-Rottweil A.-G.; *Brit. Chem. Abs.*, B, 1927, 387.

<sup>97</sup> German P. 359,583, 1920, to Farb. vorm. Meister, Lucius, & Brining; *J.S.C.I.*, 1923, 42, 69A.

<sup>98</sup> F. W. Wagner, U. S. P. 1,534,554 and 1,534,555. Apr. 21, 1925, to Jones & Laughlin Steel Corp.; *Chem. Abs.*, 1925, 19, 1773.

Plastic materials have been prepared by Hoelzer<sup>99</sup> by heating under pressure either coal tar, lignite tar, or cumarone resin, together with a sulphurous solution obtained by extracting spent gas-purification materials with carbon disulphide or tar oils. Sulphuric acid, caustic soda, ferric chloride or manganous sulphate is used as a catalyst. The resulting product is recommended for lacquers, binding agents, or covering materials.

Tar oil (freed from pitch) is converted into a resin solution, by heating it with 1 per cent of concentrated sulphuric acid.<sup>100</sup> This solution can be used directly as a varnish or paint, or it can be mixed with other resins, asphalt, linseed oil or pigments.

Resinous bases were obtained by Wirth<sup>101</sup> from coal-tar and other tar oils boiling above 300°C. The tar, previously freed from phenols, is treated with caustic soda. The aqueous solution is separated, and the remaining material is treated with dilute sulphuric acid (sp. gr. 1.12). After removal of sulphates, the mixture is cooled and the resin is separated from the tar and washed with water.

The phenols from a low-temperature tar have been made to yield a resinous product by subjecting them to a cracking process, subsequently fractionating the end-products and polymerizing the appropriate fraction.<sup>102</sup> The material obtained is a yellow, hard resin.

It has often been observed that the wash-oil used in benzol-recovery plants has a tendency to thicken. Kattwinkel<sup>103</sup> attributed this thickening to the polymerization of unsaturated compounds under the influence of heat and of sulphuric acid, the latter being formed by the oxidation of hydrogen sulphide by air in the wash oil. Offe<sup>104</sup> disagreed with this explanation, stating that the thickening is caused by the combination of hydrogen sulphide with unsaturated constituents of the wash oil. By adding paraffin oil, benzol or light petroleum to spent wash-oil a thick pitch is obtained, containing 6-11 per cent sulphur.<sup>105</sup>

<sup>99</sup> H. W. Hoelzer, British P. 331,846, 1929, to Frankfurter Gasges.; *Chem. Abs.*, 1931, 25, 223

<sup>100</sup> German P. 570,486, 1931, to Firma P. Lechler; *Chem. Abs.*, 1933, 27, 2571. British P. 379,632, 1932; *Chem. Abs.*, 1933, 27, 4107.

<sup>101</sup> E. Wirth, U. S. P. 1,339,310, May 4, 1920; *Chem. Abs.*, 1920, 14, 1894. German P. 303,273, 1915, and 304,306, 1916; *J.S.C.I.*, 1920, 39, 184A.

<sup>102</sup> W. Gluud and P. K. Breuer, *Ges. Abhandl. Kermitus Kohle*, 1919, 3, 238; *J.S.C.I.*, 1920, 39, 262A.

<sup>103</sup> R. Kattwinkel, *Gas-u. Wasserfach*, 1924, 67, 474; *J.S.C.I.*, 1924, 43, 776B. See also O. Kruber, *Brennstoff-Chem.*, 1932, 13, 187; *Chem. Abs.*, 1932, 26, 4180

<sup>104</sup> G. Offe, *Gas-u. Wasserfach*, 1923, 67, 67; *J.S.C.I.*, 1924, 43, 242B

<sup>105</sup> G. Offe, *Gas-u. Wasserfach*, 1925, 68, 136; *J.S.C.I.*, 1925, 44, 306B. R. Kattwinkel, *Brennstoff-Chem.*, 1934, 15, 141; *Brit. Chem. Abs. B*, 1934, 563.

## Chapter 7

### Applications of Cumarone Resins

Cumarone resin<sup>1</sup> is employed for a variety of purposes, particularly in the manufacture of varnishes, printing inks, waterproofing materials, rubber compositions, floor tiles and chewing gum. Although its application is in certain measure restricted, the field of utility of this resin is being continually extended. The production of cumarone in the United States has usually been in excess of demand. The resin was utilized in Germany during the War to replace natural resins to a great extent<sup>2</sup> but since that time its use and production have diminished considerably. Manufacturers have striven to produce a material having a high melting point and as little color as possible and have been so successful in their efforts that the modern product is very uniform in quality and competes in a limited way with rosin ester in the preparation of varnishes.<sup>3</sup>

#### COMMERCIAL CUMARONE RESIN

Cumarone resin is a technical product of uniform properties. The highest grade resin is sold as a clear solid (in lumps or flakes) melting above 130°C. and having a pale amber color. The material is classified according to its melting (or softening) point, and in order to obtain lower grade products of a standard quality some manufacturers prefer to "cut back" a high-grade resin by the addition of softening agents.

**Grading.** In the United States, five different grades of cumarone resin are recognized as follows:

Rubber Grade S . . .	Melting point 50°-65°C.
Medium Soft . . .	Melting point 65°-85°C.
Rubber Grade H . . .	Melting point 85°-100°C.
Medium Hard . . .	Melting point 100°-135°C.
Varnish Grade . . .	Melting point 135°-160°C.

Besides the above grades, one company produces a hard and high-melting resin recommended for use in the manufacture of wax mixtures, quick-drying varnishes, and insulating compositions. This material, which is called "Indene resin," is said to consist essentially of polymerized indene. It has a melting point of 150-160°C.<sup>4</sup>

The color of cumarone resin, which is of importance in many of its applications, has been greatly improved with the development of the technic of manufacture so that most modern grades of resin are clear and of pale color, comparable with N rosin.<sup>5</sup> The color of the resin is usually compared arbitrarily with the color of the various grades of rosin.

<sup>1</sup> One brand of cumarone resin on the market is sold as "Cumar."

<sup>2</sup> W. Fahrion, *Chem. Umschau*, 1922, 29, 103, 111, 120; *Chem. Abs.*, 1922, 16, 2419. E. Glaser, *Brennstoff-Chem.*, 1921, 2, 99, 113; *Chem. Abs.*, 1921, 15, 2362.

<sup>3</sup> Technical applications of cumarone resin are reviewed by M. Brequet, *Industrie Chimique*, Feb. 1929; *Bull. federation ind. chim. Belg.*, 1929, 8, 272. T. H. Barry, *Ind. Chemist*, 1927, 3, 479; *Chem. Abs.*, 1928, 22, 878. J. Scheiber, *Farbe u. Lack*, 1931, 170; *Chem. Abs.*, 1931, 25, 3501.

<sup>4</sup> In other respects this "Indene Resin" is very similar to the mixed cumarone-indene resins.

<sup>5</sup> The resin is obtained in flake form by spreading in a thin layer on a cooling roll and removing with a scraper; S. P. Miller, U. S. P. 1,431,676, Oct. 10, 1922; *Chem. Abs.*, 1922, 16, 4258.

In Germany<sup>6</sup> the softening point of cumarone resin is used as a criterion for grading the resin according to the following classification:

Hard and brittle	Softening above 50° C
Hard	Softening between 40° and 50° C
Medium hard	Softening between 30° and 40° C
Soft	500 or more seconds for nail test <sup>7</sup>
Viscous	100 to 500 seconds for nail test
Liquid	Less than 100 seconds for nail test.

The last two classes, strictly speaking, are resins of the synthetic balsam type and are included because of their source of supply. Each of the above classes is sub-divided according to the color of the resin into five different grades, namely, light, light-brown, brown, dark-brown and black. The standard used for grading the color of the resins is a solution containing 1.5 grams of potassium dichromate in 100 cc. of 50 per cent sulphuric acid. Comparison is made against a solution of the resin in benzene, using a colorimeter or standard tubes and viewing a cross section of the liquids with the sky as a background. The color is graded as follows:

Light	When a 10 per cent solution is not darker than the standard.
Light Brown	When a 3.5 per cent solution is not darker than the standard.
Brown	When light shows through a 10 per cent solution.
Dark Brown	When light shows through a 5-10 per cent solution.
Black	When light does not show through the solution <sup>8</sup>

**Hardness.** According to Marcusson,<sup>9</sup> the hardness of cumarone resin is inversely proportional to the amount of resin soluble in an ether-alcohol mixture. That is, very hard resins contain substances soluble in an ether-alcohol mixture to the extent of 47 to 48 per cent, hard resins contain 56 to 58 per cent of soluble material, medium hard resins contain 66 to 68 per cent, soft resins contain 70 to 85 per cent, and fluid products contain 93 to 95 per cent of soluble substances. Glaser<sup>10</sup> also stated that the most desirable resins are those having from 40 to 50 per cent of material soluble in ether-alcohol solution. Modern, high-grade resins include very little material soluble in alcohol.

**Solubility of Cumarone Resin.** Cumarone resins are soluble in a large number of organic solvents,<sup>11</sup> benzene, toluene, solvent naphtha and turpentine being the best.<sup>12</sup> The solubility varies somewhat with the melting point of the resin, lower-melting resins being rather more soluble than resins of higher melting point. Cumarone resin is also soluble in ethyl acetate, amyl acetate, acetone, butyl oxalate, butyl acetate, carbon bisulphide, carbon tetrachloride, trichloroethylene, ethyl abietate, tricresyl phosphate, and all the ethers of ethylene glycol except the methyl ether.<sup>13</sup> It is partly soluble in varnish makers' and painters' naphtha and gasoline, and entirely so if a small proportion of benzene, acetone, or butylglycol- $\beta$ -ethyl ether is added.<sup>14</sup> It is also partially dissolved by diacetone

<sup>6</sup> E. Glaser, *Brennstoff-Chem.*, 1921, 2, 113; *Chem. Abs.*, 1921, 15, 2362

<sup>7</sup> The "nail test" is designated as the time required for a 130 mm wire nail (23-24 g.) to sink from point to head at 20°C. J. Marcusson, *Chem.-Ztg.*, 1919, 43, 109, 122; *Chem. Abs.*, 1919, 13, 2607

<sup>8</sup> The last three grades are determined by viewing the benzene solution of the resin in a tube 15 mm. in diameter. The tubes are placed in a box with appropriate apertures and viewed against a 50 candlepower light.

<sup>9</sup> J. Marcusson, *Chem.-Ztg.*, 1919, 43, 109, 122; *Chem. Abs.*, 1919, 13, 2607.

<sup>10</sup> E. Glaser, *loc. cit.* See also reviews by M. Ragg, *Farben-Ztg.*, 1919, 25, 16, 61, 105, 145; *Chem. Abs.*, 1920, 14, 642. L. Clement and C. Riviere, *Chimie et Industrie*, 1922, 8, 38; *Chem. Abs.*, 1922, 16, 3404. W. Urbanus, *Kunststoffe*, 1926, 16, 175. R. Chesneau, *Bull. soc. ind. Rouen*, 1930, 58, 392; *Chem. Abs.*, 1931, 25, 3183. W. E. von Gronow, *Kunststoffe*, 1932, 22, 49; *Chem. Abs.*, 1932, 26, 2878.

<sup>11</sup> M. Bottler, *Kunststoffe*, 1915, 5, 277; *Chem. Abs.*, 1916, 10, 697.

<sup>12</sup> A. Eichler, U. S. P. 1,133,432, Mar 30 1915; *Chem. Abs.*, 1915, 9, 1398.

<sup>13</sup> It is also soluble in 1,4-dioxane. E. W. Reid and H. E. Hofman, *Ind. Eng. Chem.*, 1929, 21, 695

<sup>14</sup> French P. 771,863, 1934, to Alexander Wacker Ges für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1935, 29, 1537.

alcohol, ethyl lactate and ethyl phthalate. Petroleum distillates (particularly those derived from asphaltic base) boiling between about 155 and 210°C. exert a considerable solvent action, but the resin is less soluble in light petroleum benzines or in higher-boiling fractions. The softer grades of cumarone resin blend with paraffin oil in amounts up to 50 per cent; the harder grades blend in mixtures containing less than 5 per cent or more than 80 per cent of paraffin oil to give clear solutions. Most of the vegetable and animal oils, including menhaden oil, perilla oil, rapeseed oil, tung oil, linseed oil and soya bean oil, also pine oil and rosin oil, are solvents for cumarone resin in all proportions. The resin is less soluble in bodied oils and still less so in blown oils. It is miscible in all proportions in stearic acid, ozokerite, gilsonite, Japan wax, carnauba wax, and beeswax. In ceresin wax, and in hard paraffin wax, however, cumarone resin is only partially miscible, and it is not soluble in low-melting paraffin wax.

Cumarone resin is practically insoluble in methyl, ethyl, or amyl alcohols, or in butyl phthalate, castor oil, and diethylene glycol. Certain modified cumarone resins (prepared by the action of sulphuric acid on solvent naphthas containing phenols as well as cumarone and indene),<sup>15</sup> soluble in ethyl and similar alcohols have, however, been described.

Solutions of cumarone resin are considerably more viscous than the corresponding ones of rosin and rosin ester. To obtain solutions of similar viscosity it is necessary to use approximately 1.7 times the amount of solvent required for the preparation of rosin or rosin ester solutions of corresponding viscosity.

**General Chemical Characteristics.** Cumarone resin is distinguished from many natural and some synthetic resins by the fact that it is quite neutral and almost completely non-saponifiable. It appears to possess some unsaturation, and iodine numbers of 38 to 43.5 have been obtained with resins from one source. Objectionable impurities, such as sodium sulphate, sodium sulphonates, and free sulphonic acids are sometimes present but the best-grade products contain such materials in very minute quantities. The resin is unaffected by water, most acids, alkalis or salts and is fairly resistant to oxidation. On heating to temperatures above about 300°C., however, it undergoes partial depolymerization.

#### CUMARONE RESIN IN VARNISH MAKING

The application of cumarone resin in the form of a solution as a protective coating for wood and metal was first suggested by Kraemer and Spilker.<sup>16</sup> Since then a number of variations in the solvents employed and in the purposes for which the solution is to be used have been proposed. Cumarone resin is used to some extent in the preparation of oil varnishes such as floor, spar or rubbing varnishes, particularly in conjunction with linseed oil and tung oil. When properly made the resulting varnishes are equal for some purposes to those made from ester gum and certain of the fossil resins. Kappelmeier<sup>17</sup> points out, however, that the low durability and elasticity of cumarone resin films is a decided drawback.

Cumarone resin, used with a solvent has also been suggested as a substitute for linseed oil in varnishes.<sup>18</sup> According to Emery,<sup>19</sup> the neutral character of the resin is a disadvantage in using it alone as a varnish resin and the most satisfactory varnishes of the kind are made on the basis of 50 per cent rosin and 50

<sup>15</sup> German P. 302,543, 1917, to Rütgerswerke A.-G.; *J.S.C.I.*, 1920, 39, 307A. See Chapter 6.

<sup>16</sup> G. Kraemer and A. Spilker, *Ber.*, 1890, 23, 78; *J.S.C.*, 18'0, 58, 496.

<sup>17</sup> C. P. A. Kappelmeier, *Chem. Weekblad*, 1934, 31, 423.

<sup>18</sup> M. Darrin, U. S. P. 1,315,658, Sept. 9, 1919, and 1,382,345, June 21, 1921; *Chem. Abs.*, 1913, 13, 3027; 1921, 15, 3560. E. Stein, German P. 345,816, 1919; *J.S.C.I.*, 1922, 41, 224A.

<sup>19</sup> R. L. Emery, *Paint, Oil, Chem. Rev.*, 1929, 87 (3), 9, 21. R. S. Green, *Amer. Paint J.*, 1930, 14 (15), 20; *Paint, Oil, Chem. Rev.*, 1930, 89 (5), 11; *Chem. Abs.*, 1930, 24, 1234. W. W. King, *Paint, Oil, Chem. Rev.*, 1921, 72 (10); *Chem. Abs.*, 1921, 15, 3909.

per cent cumarone resin. The chief objection is the tendency to form a darker-colored product. A varnish which dries to a hard film in 3 to 4 hours can be obtained by adding rosin to China wood oil at 296°C., and cumarone resin at 232°C., together with driers consisting of 0.06 to 0.12 per cent of cobalt acetate and 1 per cent of lead oxide based on the weight of oil used.

In the preparation of "long oil" varnishes with tung oil it is usually necessary to add a moderate quantity of rosin as well as cumarone resin since the latter does not exert as great a solvent action on the polymerized oil as the rosin. Furthermore, it has been reported that the rate of oxidation of tung oil is much slower in cases where the oil is bodied with cumarone resin alone.<sup>20</sup> According to Kenny<sup>21</sup> cumarone resin is just as effective as limed resin in retarding the gelation of tung oil. Rapid-drying varnishes yielding promising films were produced by Rhodes and Potts<sup>22</sup> by bodying tung oil in the presence of small amounts of glycerol (to retard gelation) and 0.02 per cent of lead linoleate. After heating at 280°C. until the oil was sufficiently thickened, the cumarone resin was added and the mixture thinned with turpentine. When using lead as a drier for varnishes containing cumarone resin it is best employed in the form of the resinates, as otherwise the lead is precipitated on standing, because of the low acidity of the composition. Buc<sup>23</sup> prepared a varnish containing from 50 to 90 per cent of linseed or tung oil, 5 to 25 per cent of resins (ester gum, cumarone resin or fossil resins) and 5 to 25 per cent of the calcium salt of an oil-soluble sulphonic acid of the kind produced by treatment of petroleum oil with fuming sulphuric acid. The varnish is thinned with turpentine. Addition of the latter substance is often necessary to prevent clouding of cumarone-resin varnishes having only small proportions of rosin derivatives.

According to King,<sup>24</sup> a high-grade varnish can be produced by heating a drying oil such as tung oil to about 470°F., adding cumarone resin, and heating to about 530° until the mixture has such a consistency that it will set when cold. Additional cumarone resin may be added while the mixture is hot and thinners are added on cooling. Typical formulas suggested by King are those given in Table 20

TABLE 20 —Cumarone Resin Varnishes

Formula	Short-Oil	Medium-Oil	Long-Oil
Tung oil. . . . .	100 pounds	125 pounds	150 pounds
Linseed oil . . . . .	—	18 pounds	75 pounds
Cobalt linoleate . . . . .	1 pound	1½ pounds	2½ pounds
Cumarone resin.. . . .	100 pounds	100 pounds	100 pounds
Thinner . . . . .	200 pounds	300 pounds	380 pounds
Natural resin*. . . . .	—	—	75 pounds

\* Vegetable resin i. e., rosin or copal.

Additional formulas for the preparation of various types of varnishes are given below. It should be understood, however, that in the manufacture of varnishes the character of the oils, driers and thinners employed must be taken into consideration, as well as the technic of the varnish maker. The formulas included here serve simply as a starting point and the precise quality, or combination of qualities, sought may demand special consideration in each case. With slight changes in the proportions of oil and variations in the temperature control, satisfactory compositions for many purposes can be made. In some cases the products prepared from cumarone resin exhibit a tendency to turn yellow on exposure

<sup>20</sup> F. H. Rhodes and T. T. Ling, *Ind. Eng. Chem.*, 1925, 17, 508.

<sup>21</sup> J. A. Kenny, *Am. Paint. J.*, 1930, 14 (12), 20; *Paint. Oil, Chem. Rev.*, 1930, 89 (2), 12; *Chem. Abs.*, 1930, 24, 1234. H. Hadert, *Farbe u. Lack*, 1928, 558; *Chem. Abs.*, 1929, 23, 721.

<sup>22</sup> F. H. Rhodes and T. J. Potts, *Chem. Met. Eng.*, 1923, 29, 535.

<sup>23</sup> H. E. Buc, U. S. P. 1,735,493, Nov. 12, 1929, to Standard Oil Development Co.; *Chem. Abs.*, 1930, 24, 739.

<sup>24</sup> W. W. King, U. S. P. 1,587,333, June 1, 1926, to Barrett Co.; *Chem. Abs.*, 1926, 20, 2410.

to the weather. Although this feature is not objectionable in many instances, it should be borne in mind when the manufacture of white enamels, or other light-colored shades, is contemplated. The tendency of the coatings to become yellow is accentuated by the action of light, an exposure of twenty-four hours serving to develop the maximum color. This discoloration, however, is only of minor degree and negligible in most applications.

**Spar Varnish.**<sup>25</sup> Long-oil or spar varnishes have been prepared using cumarone resin and as an example the following formula is given:

Twenty gallons of tung oil and 20 pounds of resin are heated to 280°C. and then drawn off the fire. When a test sample strings, 10 gallons of linseed oil are introduced to chill the mixture. One hundred pounds of cumarone resin are then added and the mixture heated to 266°C. and maintained at this temperature for 15 to 30 minutes. The batch is then cooled and 2.5 pounds of cobalt linoleate are added, followed by 40 gallons of a solvent such as turpentine, naphtha, benzene, or a mixture of these solvents. The use of such a comparatively large proportion of linseed oil is advantageous in that a more elastic varnish is obtained.

Another long-oil varnish which gives free-flowing coatings may be prepared by adding 26 pounds of ester gum and 44 pounds of hard cumarone resin to 38 gallons of tung oil at 205°C. The batch is heated so as to obtain a top temperature of about 290°C. in 30 minutes and as soon as the correct consistency is attained, 4 pounds of fused lead resinate and 26 pounds of cumarone resin are added. Sufficient bodied linseed oil (about 7 gallons) is introduced to cause the temperature to drop to about 250°C. The varnish is thinned with 72 gallons of mineral spirits. Liquid driers containing cobalt and manganese are added at 175°.

**Floor Varnish.** The following is a representative formula for the preparation of medium-oil or floor varnishes:

Cumarone resin . . . . .	100.0 pounds
Tung oil . . . . .	15 5 gallons
Linseed oil . . . . .	2 5 gallons
Cobalt linoleate . . . . .	1.5 pounds
Thinner . . . . .	34.0 gallons

The tung oil is heated to about 245°C and one-half to three-quarters of the cumarone resin is added while the mixture is still on the fire, with sufficient stirring to prevent the resin from sticking to the bottom and sides of the kettle with consequent darkening of the varnish. The temperature is raised to 280°-293°C. and the kettle contents maintained at this temperature for 15 to 30 minutes or until a drop on a cold glass sets to a fairly hard button (the mixture should, however, not string). The remainder of the cumarone resin and all the linseed oil are added with stirring to check the heat. The mixture is allowed to cool and the thinner and drier added. The resulting varnish is reported to be quick-drying, tough, resistant to acids and alkalies and is waterproof.

Varnishes prepared at temperatures of about 280°C. sometimes show a slight bloom. In such cases it is better to work at somewhat higher temperatures, about 295°. The resulting products are slightly darker than those obtained at the lower temperature but the waterproofing qualities are said to offset this disadvantage. It should be borne in mind that cumarone resin darkens rapidly above 280°C. and it is therefore necessary to "body" the oil as much as possible before the resin is added in order to avoid exposure to a high temperature for too long a period. If the varnishes are made at 260°C., the resin has a tendency to fall out. On the other hand, if heating is carried above 300°C., the resulting material will be considerably darker than varnishes properly prepared from the usual natural resins.

<sup>25</sup> Typical varnish formulas in which cumarone resin is employed have been described by J. A. Kenny, *Am. Paint J.*, 1930, 14 (12), 20, 22, 24, 26; *Paint, Oil, Chem. Rev.*, 1930, 89 (2), 12; *Chem. Abs.*, 1930, 24, 1234; R. S. Green, *Am. Paint J.*, 1930, 14 (15), 20, 22, 24, 26; *Paint, Oil, Chem. Rev.*, 1930, 89 (5), 11; *Chem. Abs.*, 1930, 24, 1234; and E. E. Walker, *Times Trade and Eng. Suppl.*, 1931, 28 (664), 7; *Chem. Abs.*, 1931, 25, 2863.

**Short-Oil Varnish.** The following formula may be used for short-oil or rubbing varnishes:

Cumarone resin . . . . .	100 pounds
Tung oil . . . . .	12 gallons
Cobalt linoleate . . . . .	14 ounces
Thinner . . . . .	28 gallons

The procedure and preparation of this type of varnish is similar to that of medium-oil varnishes. The kettle is drawn from the fire and held until a sample, when cold, sets to a hard button. The resulting product has good flow and can be polished when dry without sweating.

Another formula for a short-oil varnish is as follows: Ten gallons of tung oil are heated to 204°C. and 30 pounds of cumarone resin added. The batch is heated to 290°C. and maintained at that temperature until a test shows that the desired consistency has been attained. Then 70 pounds more of cumarone resin are added to chill the mixture. As soon as the resin has completely dissolved, 25 gallons of mineral spirits are added and a liquid cobalt drier (0.10 per cent metal based on weight of oil) at 175°.

By mixing about 2 pounds of aluminum powder per gallon of a varnish prepared with cumarone resin as a constituent, fairly good waterproof coatings can be made. For interior work, a short-oil varnish of the type already described meets many requirements; however, for exterior application on steel tanks and structural steel, a long-oil varnish is of course more desirable.

Another application of cumarone resin in the varnish industry is its use as a modifying agent for oil-soluble resins of the phenol-formaldehyde type.<sup>26</sup>

Wrinkle-finish varnishes were made by Root<sup>27</sup> by use of Congo resin and blown linseed oil. Cumarone resin as a hardening agent in this type of finish was later described by Burgman.<sup>28</sup>

A representative composition may be prepared by adding a pigment (5 lb.), japan drier (3 gal.), cumarone varnish (6 gal.) and benzene (10 gal.) to a varnish base (40 gal.) comprising tung oil, 5 to 10 per cent of rosin based on the weight of oil, and cooled with the weight equivalent of high-flash naphtha. The composition is applied and subsequently baked.

**Lacquers.** Cumarone resin is not compatible with nitrocellulose and cannot be used in lacquers as the sole resin.<sup>29</sup> However, if a mutually tolerant resin is also present, the cumarone blends and a clear film is produced on drying. According to Rogers and Banta,<sup>30</sup> a ratio of 7 parts of ester gum to 4 parts of cumarone resin produces a durable lacquer.<sup>31</sup> A typical formula contains the following ingredients expressed in per cent by weight:<sup>32</sup>

Nitrocellulose ( $\frac{1}{2}$ sec., wet with 30 per cent of alcohol) . . . . .	8
Butanol . . . . .	10
Toluene . . . . .	31
Ethyl acetate . . . . .	10
Butyl acetate . . . . .	25
Dibutyl phthalate . . . . .	5
Ester gum . . . . .	7
Cumarone resin . . . . .	4

<sup>26</sup> I. Rosenblum, British Patent 416,476, Sept. 10, 1934; *Chem. Abs.*, 1935, 29, 1176. French Patent 738,444, 1932; *Chem. Abs.*, 1933, 27, 1775. See Chapter 19.

<sup>27</sup> F. B. Root, U. S. P. 1,732,661, Oct. 22, 1929, to Flood & Conklin Co.; *Chem. Abs.*, 1930, 24, 252.

<sup>28</sup> G. H. Burgman, U. S. P. 1,934,034, Nov. 7, 1933, to G. J. Liebich Co.; *Chem. Abs.*, 1934, 28, 662.

<sup>29</sup> A. Jones (*Ind. Finishing*, 1932, 3, 156; *Chem. Abs.*, 1932, 26, 5775) has discussed cumarone lacquers.

<sup>30</sup> A. Rogers and C. Banta, *Ind. Eng. Chem.*, 1928, 20, 198. A. Rogers, U. S. P. 1,884,225, Oct. 25, 1932, to Barrett Co.; *Chem. Abs.*, 1933, 27, 1219.

<sup>31</sup> The durability of colored lacquers containing various synthetic and natural resins has been investigated by H. A. Gardner, *Tech. Circ., U. S. Paint Mfrs' Assoc.*, 1925, 252, 168; *Chem. Abs.*, 1926, 20, 1145.

<sup>32</sup> R. L. Emery (*Paint, Oil, Chem. Rev.*, 1929, 87 (3), 9, 21) has advocated the use of xylene instead of toluene in the preparation of cumarone resin lacquers.



The cotton is placed in a convenient container for mixing, and butanol and toluene added. When thoroughly wetted, ethyl acetate, butyl acetate and dibutyl phthalate are introduced and the mass is stirred until dissolved. The mixture of ester gum and cumarone resin is now added and dissolved by continued stirring.

Cotton<sup>33</sup> stated that cumarone resin gives lacquers which tend to blush but that this tendency is eliminated by its partial replacement by gutta-percha resin.

Coating compositions and plastic products from cellulose esters are said to be improved by the addition of small quantities of cumarone resin.<sup>34</sup> Lacquers have also been suggested from cellulose derivatives such as acetylcellulose using cumarone resin and various solvents.

Solutions of cumarone resin have been recommended as components in the preparation of bronzing liquids.<sup>35</sup> The addition of a small quantity of stearic acid to such solutions has also been proposed.<sup>36</sup>

As a substitute for pyroxylin lacquers, Kessler<sup>37</sup> proposed to employ cumarone resin softened by tung oil, using as solvents mixtures of benzene and xylene, alcohol and fusel oil, or a mixture of all these thinners.

**Other Coating Compositions.** A composition for coating nails is stated<sup>38</sup> to consist of a resin of the cumarone type, melting at 105-110°C., mixed while in the molten condition with 30 per cent by weight of benzol. Lacquers said to be of value as ships' paints are prepared by Plauson<sup>39</sup> by the addition of cumarone resin, or hardened resin, to a dispersion of vulcanized rubber or balata in a low boiling saturated or chlorinated hydrocarbon solvent. The mixture is subsequently colloidized by heating to 180°C. Mention is made by Bowles<sup>40</sup> of the utilization of cumarone resin in antifouling paints, particularly for ships' plates. It is reported, however, that protective paints, made from cumarone resins, exhibit a tendency to crumble away when exposed to sea-water.<sup>41</sup>

Blass<sup>42</sup> polymerized the cumarone and indene in solvent naphtha with sulphuric acid and neutralized the free acid with dry alkalies. The resulting solution is used directly as a paint base. He suggests Portland cement as a pigment.

An application of cumarone resin is in the manufacture of an enamel or paint for coating the interior of containers used in canned foods (particularly corn). Tin-plate containers are frequently attacked with the formation of dark-colored, objectionable compounds; this discoloration is inhibited by application of one of the following mixtures:

(1) Cumarone resin, 10 parts, and zinc oxide, 5 parts.

(2) Cumarone resin, 18 parts, gutta-percha 4 parts, and zinc oxide, 11 parts.

(3) Cumarone resin, 18 parts, chicle gum, 4 parts, and zinc oxide, 11 parts.

In making up the compositions, the cumarone resin, chicle gum, and gutta-percha are dissolved in about 5 parts by weight of carbon tetrachloride and zinc oxide is stirred in. After the mixture has been passed twice through a paint mill, sufficient carbon tetrachloride is added to reduce the total solids to about 5 per cent. This composition is applied to the cans and baked.<sup>43</sup>

<sup>33</sup> F. H. Cotton, *India Rubber J.*, 1929, 78, 531; *Chem. Abs.*, 1930, 24, 525.

<sup>34</sup> F. Lehmann and J. Stocker, U. S. P. 1,185,514, May 30, 1916 and 1,191,801, July 18, 1916; *Chem. Abs.*, 1916, 10, 1939, 2299. German P. 281,265, 1913, to Zapon-Lac. G.m.b.H.; *Chem. Abs.*, 1915, 9, 1850. F. Lehmann, French P. 471,104, 1914; *J.S.C.I.*, 1914, 33, 187.

<sup>35</sup> M. Fehringer, U. S. P. 1,157,768, Oct. 26, 1915; *Chem. Abs.*, 1915, 9, 3369. W. B. Roberts and J. D. Edwards (*Off. Digest, Fed. Paint, Varnish Prod. Clubs*, 1934, 134, 61; *Chem. Abs.*, 1934, 28, 3252) use a solution of cumarone resin in mineral spirits (30 g. to 100 cc.) in determining the leafing properties of aluminum-bronze powder.

<sup>36</sup> J. G. Shilvock, U. S. P. 1,411,673, Apr. 4, 1922; *Chem. Abs.*, 1922, 16, 2035.

<sup>37</sup> J. M. Kessler, U. S. P. 1,411,035, Mar. 28, 1922; *Chem. Abs.*, 1922, 16, 1875.

<sup>38</sup> S. I. Charlesworth and A. W. Harris, U. S. P. 1,782,341, Nov. 18, 1930; *Chem. Abs.*, 1931, 25, 424.

<sup>39</sup> H. Plauson, British P. 326,216, 1928; *Brit. Chem. Abs. B*, 1930, 520.

<sup>40</sup> E. E. Bowles, *J.S.C.I.*, 1922, 41, 494R.

<sup>41</sup> A. Pignot, *Rev. Met.*, 1929, 26, 310; *Brit. Chem. Abs. B*, 1929, 721.

<sup>42</sup> T. Blass, U. S. P. 1,401,034, Dec. 20, 1921, to W. H. Ahlbert; *Chem. Abs.*, 1922, 16, 1018.

<sup>43</sup> G. S. Bohart, *Nat. Canners Assoc. Res. Lab. Circ. No. 10L*, 1924; *Chem. Abs.*, 1925, 19, 2857. U. S. P. 1,699,274, Jan. 15, 1929, to Nat. Canners Assoc.; *Chem. Abs.*, 1929, 23, 1185.

Steigerwalt<sup>44</sup> has reported that cumarone resin is apparently unaffected by immersion in acetic or lactic acid. On the basis of such tests he suggested that the resin, in conjunction with emulsified asphalts, rubber or Portland cement, be employed as a coating for silos.

Solutions of cumarone resin have been used for a wide variety of purposes, particularly for the production of waterproofing compositions and adhesive mixtures. A dilute solution of the resin in benzene or toluene containing an oil-soluble dye has been recommended for tinting cloth exposed to the weather, such as the lining of automobile tops.<sup>45</sup> Chabert<sup>46</sup> impregnated textile fibers by dipping them into a bath containing cumarone resin, hydrogenated fish oil, a solvent of the type of mineral spirit, and acetone. A waterproofing composition for use on leather, canvas, or other fabric, and also for rust-proofing metal, was prepared by Shaffer<sup>47</sup> by mixing a solution of cumarone resin (preferably of high melting point) in high-flash naphtha, with one of paraffin wax and rubber cement in gasoline. According to Crawford,<sup>48</sup> 50 parts of cumarone resin and 40 parts of carnauba wax incorporated with 20 parts of linseed oil at 177-204°C. with constant agitation for 45 minutes gives a preparation for coating electrical coils. Compositions containing the resin for the waterproofing of leather<sup>49</sup> and paper<sup>50</sup> have also been described. In the case of leather, paraffin wax is mixed with 5-30 per cent of rubber or gutta-percha and a small amount of cumarone resin. Application is made at 95°C. Waterproof paper is manufactured in such a way that the resin along with menhaden oil is distributed between the fibers.

The unsaponifiable nature of cumarone resin has led to its employment in solvents or compositions for waterproofing cement floors and in the manufacture of cement binders.<sup>51</sup> Water-immersion tests on concrete panels coated with a cumarone resin varnish and then painted with chrome green showed the varnish to be outstanding in its preventing attack of Prussian blue in the paint.<sup>52</sup>

Fleischmann<sup>53</sup> obtained a waterproof floor-covering cement by dissolving one part by weight of a high-melting cumarone resin in about 0.25 to 2 parts of benzol and incorporating from 0.5 to 4 parts of a clay filler. Still another use has been proposed by McCoy,<sup>54</sup> who impregnated molded articles made of Portland cement or asbestos with a solution of cumarone resin to render them more adaptable for use in the manufacture of electrical apparatus. The articles are then baked.

Ellis<sup>55</sup> prepared a quick-drying paint, which dries to a flat or dull finish and can be applied to wall plaster or other surfaces to produce a flat waterproof finish, by dissolving cumarone resin of melting point about 90°C. in a mixture of about 9 parts of gasoline and 1 part of toluene and incorporating a pigment such as lithopone, iron oxide, ochre or Brunswick green.

<sup>44</sup> G. F. Steigerwalt, *Agr. Eng.*, 1933, 14, 154; *Chem. Abs.*, 1934, 28, 873.

<sup>45</sup> Carleton Ellis, U. S. P. 1,412,014, Apr. 4, 1922; *Chem. Abs.*, 1922, 16, 2032.

<sup>46</sup> F. Chabert, French P. 38,522, 1930; addn. to 683,946; *Chem. Abs.*, 1932, 26, 1135.

<sup>47</sup> C. D. Shaffer, U. S. P. 1,583,191, May 4, 1926 and 1,441,805, Jan. 9, 1923, to Textile, Leather & Metal Preserver Co.; *Chem. Abs.*, 1926, 20, 2052.

<sup>48</sup> C. A. Crawford, U. S. P. 1,691,543, Nov. 13, 1929; to Western Electric Co.; *Chem. Abs.*, 1929, 23, 532.

<sup>49</sup> E. D. Van Tassel, British P. 298,062, 1927, to Van Tassel Co.; *Chem. Abs.*, 1929, 23, 1523.

<sup>50</sup> C. J. Strobel and A. P. Tallman, U. S. P. 1,803,816, May 5, 1931; *Chem. Abs.*, 1931, 25, 3838.

<sup>51</sup> Carleton Ellis, U. S. P. 999,493, Aug. 1, 1911 and 999,708, Aug. 8, 1911, to Ellis-Foster Co.; *Chem. Abs.*, 1911, 5, 3143. U. S. P. 1,005,818, Oct. 17, 1911; *Chem. Abs.*, 1912, 6, 163. U. S. P. 1,383,268, June 28, 1921; *Chem. Abs.*, 1927, 21, 4045. See also Carleton Ellis and H. M. Weber, U. S. P. 1,381,868, June 14, 1921, to Ellis-Foster Co.; *Chem. Abs.*, 1921, 15, 3560.

<sup>52</sup> *Circ., Nat. Paint, Varnish and Lacquer Assoc.*, 1934, 471, 297; *Paint, Oil, Chem. Rev.*, 1934, 96 (32), 78; *Brit. Chem. Abs. B.*, 1935, 32.

<sup>53</sup> L. Fleischmann, U. S. P. 1,840,637, Feb. 23, 1932; *Chem. Abs.*, 1932, 26, 2569.

<sup>54</sup> J. P. McCoy, U. S. P. 1,299,847, Apr. 8, 1919, to Westinghouse Electric & Manufacturing Co.; *Chem. Abs.*, 1919, 13, 1910.

<sup>55</sup> Carleton Ellis, U. S. P. 1,451,092, Apr. 10, 1923, to Ellis-Foster Co.; *Chem. Abs.*, 1923, 17, 2058.

Sprenger<sup>56</sup> prepared a varnish by treating (for 1 hour) oils containing cumarone and indene (to which had been added 5-10 per cent of animal or vegetable oil) with 21 per cent of concentrated sulphuric acid. The temperature was kept below 50°C. Freshly slaked lime was then added to neutralize sulphuric acid and combine with any free fatty acids. After removal of insoluble calcium salts, the varnish oil obtained was of a clear brownish-yellow color and, when applied in a thin film, dried to an elastic coating. Lender and Koch<sup>57</sup> made a varnish base by adding drying oils, natural resins or animal and vegetable waxes to a solution of cumarone-indene resin in solvent naphtha and subsequently evaporating the solvent. Another base was secured by heating tung oil to 220-240° and incorporating an equal weight of cumarone resin. For the manufacture of varnishes, Eichler<sup>58</sup> recommended the addition of linseed, poppy seed, cottonseed or soya-bean oils, in small quantities at a time, to cumarone resin heated to about 160°C. By combining heat-polymerized cumarone resin with oils such as corn oil, soya-bean oil and tung oil, Darrin<sup>59</sup> obtained a composition possessing electrical insulating properties. Edison<sup>60</sup> used a solution of the resin to coat electrodes of electroplating cells to prevent deposition of metals. Dayol<sup>61</sup> suggested a vehicle for paints consisting of a mixture of 60 per cent of cumarone resin, 40 per cent of xylene and a small amount of drier and oil of mirbane. A coating, prepared by Holzapfel,<sup>62</sup> consisted of cumarone resin and 1 to 10 per cent of rubber. Stearin pitch may also be incorporated in some cases.

Stewart<sup>63</sup> made a varnish by treating an unsaturated vegetable oil, such as tung oil, with a small proportion of phosphorus pentoxide. A gelatinous material is formed by polymerization and the mixture is immediately added to a solution of cumarone resin in linseed oil. Polymerization is completed by heating and allowing the mixture to stand. The products are said to have weather-resisting properties. Schmidding<sup>64</sup> described the preparation of lacquers by the addition of cumarone resin to tung oil which has been thickened without gelatinization (by rapid heating to 280-300°C.). Another procedure<sup>65</sup> consists in dissolving coal-tar or water-gas tar pitch in solvent naphtha and subsequently polymerizing the resins by blowing in steam at 160° or by the aid of catalysts. Lender<sup>66</sup> prepared a varnish base by heating cumarone resin (oils may be added to modify the product) with sulphur or sulphur chloride<sup>67</sup> under pressure. Schwarz<sup>68</sup> stated that a liquid applicable for use as a varnish was produced by treating hot cumarone resin with air or oxygen<sup>69</sup> under pressure and emulsifying the product with water, using glue and potassium bichromate to stabilize the emulsion. A varnish-base can be produced by heating a phenol-aldehyde resin with cumarone resin and

<sup>56</sup> O Sprenger, German P. 254,767, 1911; *Chem. Abs.*, 1913, 7, 1110.

<sup>57</sup> R. Lender and A. Koch, U. S. P. 1,019,666, Mar. 8, 1912; *Chem. Abs.*, 1912, 6, 1377. R. Lender, German P. 245,634, 1911; *Chem. Abs.*, 1912, 6, 2334. German P. 348,088, 1919, to Chem. Fabr. Worms A.-G.; *J.S.C.I.*, 1922, 41, 382A.

<sup>58</sup> A. Eichler, U. S. P. 1,133,432 and 1,133,433, Mar. 30, 1915; *Chem. Abs.*, 1915, 9, 1398.

<sup>59</sup> M. Darrin, U. S. P. 1,370,195, Mar. 1, 1921 and 1,382,345, June 21, 1921, to Koppers Co.; *Chem. Abs.*, 1921, 15, 1630, 3560.

<sup>60</sup> T. A. Edison, U. S. P. 1,364,359, Jan. 4, 1921; *Chem. Abs.*, 1921, 15, 767.

<sup>61</sup> J. M. Dayol, French P. 514,405, 1920; *Kunststoffe*, 1922, 12, 70.

<sup>62</sup> A. C. Holzapfel, U. S. P. 1,430,983, Sept. 26, 1922 and 1,431,801, Oct. 10, 1922; *Chem. Abs.*, 1922, 16, 4073, 4353.

<sup>63</sup> P. M. Stewart, U. S. P. 1,464,224, Sept. 17, 1923; *Chem. Abs.*, 1923, 17, 3261.

<sup>64</sup> W. Schmidding, British P. 247,599, 1925; *Chem. Abs.*, 1927, 21, 660.

<sup>65</sup> F. W. Sperr and M. Darrin, British P. 118,079, 1917; *J.S.C.I.*, 1919, 38, 46A. U. S. P. 1,292,907, Jan. 23, 1919; *Chem. Abs.*, 1919, 13, 1024. Cf. M. Darrin, U. S. P. 1,296,770, Mar. 11, 1919; *Chem. Abs.*, 1919, 13, 1645.

<sup>66</sup> R. Lender, German P. 277,605, 1913; *J.S.C.I.*, 1915, 34, 187. Dutch P. 138, 1914; *Z. angew. Chem.*, 1914, (2) 27, 588.

<sup>67</sup> K. Schlatter (U. S. P. 1,294,836, Feb. 18, 1919; *Chem. Abs.*, 1919, 13, 1159) used chromyl chloride.

<sup>68</sup> W. Schwarz, German P. 322,802, 1918; *Chem. Abs.*, 1921, 13, 2199.

<sup>69</sup> Knüppel, German P. 253,437, 1912; *J.S.C.I.*, 1912, 31, 1191.

wood-oil.<sup>70</sup> Such mixtures are prepared for application as varnishes or impregnating agents.<sup>71</sup>

A bituminous paint containing cumarone resin is produced by heating coal-tar pitch to 160-200°C., cooling the pitch to 150° and then adding a solvent containing the resin, or a solution of cumarone and indene which afterwards is polymerized by heating in an autoclave.<sup>72</sup>

Briggs<sup>73</sup> described an enamel consisting of cumarone resin, a pigment and an oil. This material was stated to be applicable for use as a top coating on slow-drying paints or varnishes. An elastic, waterproof coating composition (containing cumarone resin as one ingredient) intended as a surfacing compound on brick, stone or iron was prepared by Robeson.<sup>74</sup> This material consists of the resin, a mineral or vegetable wax, a solvent, a pigment and silicon carbide.

#### USES OF CUMARONE RESIN IN RUBBER COMPOSITIONS

Among the various applications of cumarone resin, its use in the manufacture of rubber goods is second to its employment in varnish making. The resin exerts a pronounced softening effect upon rubber during milling, and the addition of a small quantity (usually about 5 per cent), in either powdered or molten form, facilitates handling of the rubber batch on the rolls.<sup>75</sup> The adhesive properties of friction tape are increased by incorporation of cumarone resin. It is also a plasticizer for tire treads, sidewalls and friction stocks, helps to produce a smooth-running tube stock, and is said not to affect aging qualities. The resin may be used in making tiling, matting, hose, heels and various other types of mechanical rubber goods. Mixed with stearic acid and paraffin, it forms a flux which not only plasticizes the gum but gives the vulcanized product a glossy surface.<sup>76</sup> It can also be employed with advantage in rubber cements and gutta-percha compositions and as a softener for reclaimed rubber.<sup>77</sup> The softening action of cumarone resin may be illustrated by its proposed use in the preparation of a latex substitute.<sup>78</sup> Thus, plasticization of the rubber is accomplished with the aid of the resin and the resulting product is masticated with a stiff paste of a water-soluble organic colloid (e.g., rosin soap) containing an attriting agent.

On the other hand, it is stated<sup>79</sup> that cumarone resin is less beneficial in the curing of rubber with zinc oxide than are some of the more acidic resins (e.g., rosin or pine tar) which exert an increase in the tensile strength of rubber up to 2 per cent. This effect is probably due to the increased solubility of the zinc oxide in the presence of acids. Cumarone resin being neutral in character can have no such solvent action.

<sup>70</sup> J. Berend, British P. 15,875, 1914 to Chem. Fabr. K. Albert; *J.S.C.I.*, 1915, 34, 805. U. S. P. 1,205,081, Nov. 14, 1917; *Chem. Abs.*, 1917, 11, 216.

<sup>71</sup> A. Voss, German P. 477,226, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 4090. V. H. Turkington, U. S. P. 1,677,417, July 17, 1928, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 3307.

<sup>72</sup> F. W. Sperr and M. Darrin, U. S. P. 1,292,907 and 1,292,908, Jan. 28, 1919, to Koppers Co.; *Chem. Abs.*, 1919, 13, 1024. British P. 118,079, 1917; *J.S.C.I.*, 1919, 38, 46A; Canadian P. 118,272, 1919; *Chem. Abs.*, 1919, 13, 518. M. Darrin, U. S. P. 1,296,776, Mar. 11, 1919, to Koppers Co.; *Chem. Abs.*, 1919, 13, 1645. British P. 129,264, 1919; *J.S.C.I.*, 1919, 38, 379A. For other bituminous paints employing tar oil and cumarone resin see P. Lechler, British P. 379,632, 1932; *Brit. Chem. Abs.*, B, 1932, 987. N.-V. T. Uithoorn, Dutch P. 21,102, 1930; *Chem. Abs.*, 1930, 24, 2903.

<sup>73</sup> W. A. Briggs, British P. 168,293, 1921; *Chem. Abs.*, 1922, 16, 351.

<sup>74</sup> W. B. Robeson, U. S. P. 1,405,941, Feb. 7, 1922; *Chem. Abs.*, 1922, 16, 1328.

<sup>75</sup> J. Y. Malone (U. S. P. 1,990,996, Feb. 12, 1935; *Chem. Abs.*, 1935, 29, 2262) incorporated cumarone resin with rubber after it had been milled and aged to prepare an adhesive for glass or celluloid.

<sup>76</sup> J. J. O'Hare, U. S. P. 1,985,261, Dec. 25, 1934, to Am. Hard Rubber Prod. Corp.; *Chem. Abs.*, 1935, 29, 1284.

<sup>77</sup> H. McGee (British P. 389,873, 1931, to Improved Textile Rollers, Ltd.; *Brit. Chem. Abs.*, B, 1932, 481) reclaimed rubber by mixing the disintegrated material with cumarone oil and vulcanizing agents. The resulting mass is then molded under heat and pressure.

<sup>78</sup> H. L. Levin, U. S. P. 1,950,451, Mar. 13, 1934, to Patent & Licensing Corp.; *Chem. Abs.*, 1934, 28, 8270.

<sup>79</sup> W. F. Russell, *Ind. Eng. Chem.*, 1929, 21, 737.

According to Miller,<sup>80</sup> cumarone resin is improved for rubber-compounding purposes and the tendency to "bloom" is reduced by mixing 10-20 per cent sulphur in the molten resin. Richards and Smith<sup>81</sup> advocate the employment of the resin in the reclaiming and dispersing of vulcanized rubber.

Wells<sup>82</sup> prepared a product for making gaskets by mixing the resin with rubber and fillers, such as clay or asbestos. The material so obtained was subsequently shaped and vulcanized.

McCoy<sup>83</sup> made a cement (for sealing vacuum apparatus) by heating a mixture of 10 to 50 per cent of gutta-percha, 50 to 80 per cent of cumarone resin, and a filler such as precipitated chalk to a temperature of about 260°C. The cements may be repeatedly melted and solidified without impairing their properties and are exceedingly tough.

Rubber cements proposed as surfacing material for floors or roads, or as acid-resisting coatings, are made by mixing cumarone resin and a water-setting cement (e.g., Portland cement) with a dispersion of an aqueous liquid in rubber and allowing the composition to set. The resin counteracts any retarding effect of rubber solvent on the setting.<sup>84</sup>

An adhesive consisting of 2-5 parts of Karaya gum, 25 parts of cumarone resin, 17 parts of spindle oil and 100 parts of rubber latex (containing 33 per cent of solids) has been described.<sup>85</sup> Teague<sup>86</sup> mixed an emulsion of cumarone resin in water with rubber latex in the presence of thickening and stabilizing agents. It is stated that the best results are obtained with a resin melting at 40°C. Another procedure<sup>87</sup> consists in blending an emulsified mixture of cumarone resin and neutralized pine tar with an aqueous dispersion of rubber.

By kneading together at 140°C. 100 parts of cumarone resin and 15 parts or less of vulcanized rubber (in crumb form), Blumberg<sup>88</sup> secured a plastic material applicable for cementing and insulating purposes. The use of solvents during mixing and replacement of the cured rubber with crude or chlorinated rubber were suggested. Drew<sup>89</sup> mixed plasticized rubber (clear crepe or smoked sheets), cumarone resin and pigments such as zinc oxide. The resulting mixture is incorporated with benzene or gasoline. It may be used on paper or other material.

Paulitsch<sup>90</sup> used a preparation containing cumarone resin (40 parts), ethyl alcohol (50 parts) and potassium carbonate (10 parts) as a coating for tires and footwear.

A composition proposed by Miller<sup>91</sup> may be prepared by dissolving about 8 per cent by weight of crude unvulcanized rubber in molten cumarone resin of melting point between 125°C. and 128°. The resulting product melts at about 123° and may be used in varnishes, paints, lacquers, enamels, insulating compounds, waterproofing materials for fibrous materials and in the manufacture of linoleum.

A blend of oily distillates and still residues from coal tar has been recommended

<sup>80</sup> S. P. Miller, U. S. P. 1,782,693, Nov. 25, 1930, to Barrett Co.; *Chem. Abs.*, 1931, 25, 437.

<sup>81</sup> T. G. Richards and G. F. F. Smith, U. S. P. 1,671,316, May 29, 1928, to Dispersions Process, Inc.; *Chem. Abs.*, 1928, 22, 2886.

<sup>82</sup> A. A. Wells, U. S. P. 1,248,226, Nov. 27, 1917, to Ellis-Foster Co.; *Chem. Abs.*, 1918, 12, 323.

<sup>83</sup> J. P. McCoy, U. S. P. 1,248,226, Nov. 27, 1917, to Ellis-Foster Co.; *Chem. Abs.*, 1918, 12, 323.

<sup>84</sup> N. Swindin, British P. 339,002, 1929, to Nordag, Ltd.; *Brit. Chem. Abs. B*, 1931, 263.

<sup>85</sup> British P. 240,141, 1924, to General Rubber Co.; *Chem. Abs.*, 1926, 20, 2262.

<sup>86</sup> M. C. Teague, U. S. P. 1,719,948, July 9, 1929 to General Rubber Co.; *Chem. Abs.*, 1929, 23, 4376. British P. 240,141, 1925; *Brit. Chem. Abs. B*, 1925, 1000.

<sup>87</sup> M. C. Teague, U. S. P. 1,750,767, Mar. 18, 1930 to Naugatuck Chem. Co.; *Brit. Chem. Abs. B*, 1931, 77.

<sup>88</sup> O. Blumberg, British P. 419,496, 1934; *Brit. Chem. Abs. B*, 1935, 69. French P. 768,078, 1934; *Chem. Abs.*, 1935, 29, 522.

<sup>89</sup> R. G. Drew, U. S. P. 1,814,132, July 14, 1931 to Minnesota Mining & Mfg. Co.; *Chem. Abs.*, 1931, 25, 5258. British P. 312,610, 1928 and 405,263, 1934; *Chem. Abs.*, 1930, 24, 931; 1934, 28, 4191.

<sup>90</sup> M. Paulitsch, Austrian P. 138,640, 1934; *Chem. Abs.*, 1935, 29, 530.

<sup>91</sup> S. P. Miller, U. S. P. 1,682,397, Aug. 28, 1928 to Barrett Co.; *Chem. Abs.*, 1928, 22, 3940.

for use in rubber compositions. The addition of 2 per cent to the gum during milling aids in dispersion of fillers.<sup>92</sup> Similar use is made of mixtures of cumarone resin and coal-tar oils.<sup>94</sup>

**Chicle Substitutes.** As cumarone resin mixes with chicle, pontianak rubber, rubber resin and flavoring oils, and can be obtained free from oily substances which impart a disagreeable flavor, it has been suggested as an ingredient for chewing gum.<sup>94</sup> Generally about 7-10 per cent of the resin is incorporated with chicle. Although slight changes in the manufacture of cumarone resin have resulted in the exudation of sweetening material when it is employed as a chicle substitute, this difficulty can be overcome by careful selection of the grade of resin.

A chewing gum base material may be prepared by drying (at above 100°C.) a mixture of rubber latex, powdered cumarone resin, and hard hydrogenated oil in a mixer, kneading at 115° to 120° and adding cacao powder or other filling material.<sup>95</sup> Another method is to cream rubber latex with a solution of caustic soda, and mix the upper cream layer with cumarone resin. The mixture is heated and stirred, then the alkali is removed by washing. The residual water is evaporated and the product is blended with hard hydrogenated oil.<sup>96</sup>

#### MOLDED ARTICLES

Cumarone resin has found only a limited application in the preparation of molded articles because it is too brittle and possesses a low tensile strength. Its incorporation has been suggested in the so-called cold-molded products when mixed with other materials such as asphalt, petroleum pitch or gilsonite. Cumarone resin has found but slight application in the manufacture of hot-molded articles.<sup>97</sup> As contrasted with its disadvantages, cumarone resin possesses the property of being resistant to moisture and climatic conditions, besides possessing excellent insulating characteristics. Porcelain and gutta-percha are examples of materials possessing higher dielectric constants. Table 21 gives comparative values of the dielectric constants of cumarone resin and various other materials, measured under the same conditions.

TABLE 21.—*Dielectric Constants of Various Insulating Materials*

Substance	Dielectric Constant
Porcelain . . . . .	5.73
Gutta-percha . . . . .	4.0 to 4.9
Cumarone resin . . . . .	3.5
Shellac . . . . .	3.10
Vulcanized rubber . . . . .	2.69
Rosin . . . . .	2.5
Rubber . . . . .	2.12

The addition of cumarone resin to products made by reacting phenols with formaldehyde was proposed by Baekeland.<sup>98</sup> Resinous substances such as polymerized cumarone and indene, when mixed with Bakelite, not only control the rate

<sup>92</sup> B. F. Schwalm, U. S. P. 1,869,172, July 26, 1932, to Neville Co.; *Chem. Abs.*, 1932, 26, 5452.

<sup>93</sup> A. B. Cowdery, Canadian P. 349,513, 1935; *Chem. Abs.*, 1935, 29, 4211.

<sup>94</sup> H. M. Weber, U. S. P. 1,248,961, Dec. 4, 1917 to Ellis-Foster Co.; *Chem. Abs.*, 1918, 12, 440; U. S. P. 1,402,817, Jan. 10, 1922 to Ellis-Foster Co.; *Chem. Abs.*, 1922, 16, 996.

<sup>95</sup> F. V. Canning, U. S. P. 1,975,447, Oct. 2, 1934, to Sweets Laboratories, Inc.; *Chem. Abs.*, 1934, 28, 7448. British P. 347,376, 1930; *Brit. Chem. Abs. B.*, 1931, 696. German P. 551,961, 1930; *Chem. Abs.*, 1932, 26, 4980.

<sup>96</sup> British P. 357,350, 1930, to Sweets Laboratories, Inc.; *Brit. Chem. Abs. B.*, 1931, 1121. See also H. V. Dunham, U. S. P. 1,534,929 to 1,534,931, April 21, 1925; *Chem. Abs.*, 1925, 19, 1760.

<sup>97</sup> Cumarone has been used in thermoplastic molding compositions made from hardened shellac; W. A. Broughton, U. S. P. 1,953,951, Apr. 10, 1934, to New England Mica Co.; *Chem. Abs.*, 1934, 28, 3920. See also Chap. 37.

<sup>98</sup> L. H. Baekeland, U. S. P. 1,033,475, Sept. 10, 1912; *Chem. Abs.*, 1912, 6, 2534.

of hardening, but also facilitate molding.<sup>100</sup> In the preparation of molded articles from filler stock of asbestos, silica and wood flour, McCoy<sup>100</sup> used the resin as a binder in addition to polymerized vegetable oils, such as tung oil, or sterculia oil. The molding composition was preshaped to the desired form and then, by means of heat and pressure, formed into the finished molded article. The operation could also be carried out by the cold-molding process, but in this case less vegetable oil must be used in the composition. When shaped in the latter way, the articles are finally subjected to a baking treatment<sup>101</sup> in order to polymerize the binder.<sup>102</sup> The molded products have adequate insulating power. For cold molding, a recommended mixture consists of 70 parts of asbestos, 30 parts of cumarone resin and 1 to 2 parts of tung oil.

Wells<sup>103</sup> prepared an insulating composition by dissolving cumarone resin in a solvent such as benzene, admixing with asbestos, drying, heating, and molding the material under high pressure. The proportion of cumarone resin may be varied within wide limits, depending upon the physical qualities desired, and shellac, asphalt, or other resins may be incorporated.

By grinding a mixture of cumarone resin and filling material with water, Gudge<sup>104</sup> found that some of the difficulties encountered in using resinous binders for the preparation of molded articles could be overcome. Without the use of water, the resin sometimes "balls" with the filler or, if a ball mill is employed, the mix adheres to the sides of the mill so that mixing is not uniform.

Cumarone resin, mixed with shellac<sup>105</sup> or phenol-formaldehyde resin,<sup>106</sup> is suggested as a bonding agent for abrasive granules. The binder may be incorporated with the granules in the presence of a solvent (e.g., furfural) and the article baked.

Groten<sup>107</sup> obtained an insulating composition for use in the construction of coils and condensers for motor ignition systems by heating a mixture of 85 per cent of cumarone resin (melting at 80-100°C.) with 15 per cent of tung oil at 130° until a clear liquid results. This material, which has a melting point of about 60°, forms a permanent insulation. Magnetic cores of high permeability are produced by impregnating a metallic powder with liquid or soft cumarone resin along with asphalt and pitches.<sup>108</sup> The preparation is molded by subjecting it to pressure.

Brown<sup>109</sup> suggests adding 10-35 per cent of cumarone resin to tung oil and heating at 200-250°C. until the mixture is of the requisite body. This is applied, either directly or in solution, to fabrics which, after drying by baking, are rendered waterproof and electrically insulated. Products said to be useful as adhesive plasters and as impregnating agents have been prepared from equal parts of naphthol pitch, sesame oil and cumarone resin.<sup>110</sup>

Grant and Farren<sup>111</sup> proposed a mixture of molten cumarone resin, molten

<sup>100</sup> J. P. McCoy, U. S. P. 1,425,784, Aug. 15, 1922; *Chem. Abs.*, 1922, 16, 3354.

<sup>101</sup> J. P. McCoy, U. S. P. 1,268,031, May 28, 1918, to Westinghouse Electric & Mfg. Co.; *Chem. Abs.*, 1918, 12, 1820.

<sup>102</sup> J. P. McCoy, U. S. P. 1,300,218, Apr. 8, 1919 and Reissue 15,199, Sept. 20, 1921, to Westinghouse Electric & Mfg. Co.; *Chem. Abs.*, 1919, 13, 1909.

<sup>103</sup> J. P. McCoy, U. S. P. 1,299,846 and 1,299,847, Apr. 8, 1919; *Chem. Abs.*, 1919, 13, 1910; U. S. P. 1,245,363, Nov. 6, 1918, to Westinghouse Electric & Mfg. Co.; *Chem. Abs.*, 1918, 12, 280.

<sup>104</sup> A. A. Wells, U. S. P. 1,332,860, Mar. 2, 1920, to Ellis-Foster Co.; *Chem. Abs.*, 1920, 14, 1198.

<sup>105</sup> B. J. Gudge, U. S. P. 1,299,706, Apr. 8, 1919, *Chem. Abs.*, 1919, 13, 1910.

<sup>106</sup> H. R. Power, U. S. P. 1,427,844, Sept. 5, 1922, to Carborundum Co.; *Chem. Abs.*, 1922, 16, 3738.

<sup>107</sup> F. A. Upper, U. S. P. 1,950,641, Mar. 18, 1934, to Bakelite Corp.; *Brit. Chem. Abs. B.*, 1935, 195.

<sup>108</sup> F. J. Groten, U. S. P. 1,455,200, Mar. 15, 1923, to Connecticut Telephone & Electric Co., Inc.; *Chem. Abs.*, 1923, 17, 2335.

<sup>109</sup> British P. 320,811, 1923, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1930, 21.

<sup>110</sup> A. L. Brown, U. S. P. 1,492,155, Apr. 29, 1924, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1924, 18, 1866.

<sup>111</sup> British P. 362,034, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 171. French P. 711,790, 1931; *Chem. Abs.*, 1932, 27, 2025.

<sup>112</sup> H. L. Grant and W. R. Farren, U. S. P. 1,812,576, Dec. 28, 1926, to Atlas Powder Co.; *Chem. Abs.*, 1927, 21, 617.

sulphur and a filler of sand, clay, glass or brick dust as a waterproof and dielectric sealing material for electrical blasting caps and other protective containers for delicate electrical and mechanical units. A mixture of sulphur and a soft cumarone resin is cold molded by Herbst and Endriz<sup>112</sup> and then baked for about 16 hours at 250-260°C. to secure hard black articles reported to have high dielectric strength.

Electrically insulated compositions for the construction of partitions are made by mixing a solution of nitrocellulose, cumarone resin, shellac, copal, and tricresyl phosphate in solvents with slag wool or asbestos, and evaporating the volatile constituents.<sup>113</sup> A sound- and shock-insulating medium is composed of a vulcanized oil mixed with magnesium oxide and cumarone resin.<sup>114</sup> Textile webbing impregnated with cumarone resin was proposed by Haas<sup>115</sup> for molding into a water-lubricated bearing.

On account of its resistance to saponification cumarone resin has been proposed as a binding agent for constructional materials. Reumann<sup>116</sup> produced a composition for building and road-making purposes by adding to molten cumarone resin pieces of marble, lithopone, hard waxes and rubber. Plauson<sup>117</sup> employed cumarone resin as a dispersing agent for the hard pitch, bitumen or natural resin which are added to the tar. The resin is manufactured *in situ* by heating a mixture of tar, solvent naphtha and sulphuric acid. Another procedure involves incorporating tar with 5-20 per cent of the resin and emulsifying in hot water containing a small proportion of a soap.<sup>118</sup>

A preparation for rolling on tennis courts, footpaths or pavements is obtained<sup>119</sup> by coating sand with 5 to 6 per cent of a solution of cumarone or indene resin in a heavy petroleum distillate.

#### LINOLEUM AND OILCLOTH

In the manufacture of linoleum and oilcloth, cumarone resin is employed to some extent and the success attending its use depends largely upon the maker of the linoleum varnish composition.<sup>120a</sup>

Oilcloth is manufactured by impregnating a cotton cloth such as muslin, duck or canvas with several sizing coats made up of an emulsion of drying oil or clay, for example, in water. The coats are spread evenly on the fabric with a "doctor knife," the cloth being maintained under proper tension in order that the layers may be evenly distributed. After each sizing coat the cloth is dried before the next one is spread on. The last application may or may not contain cumarone resin, depending upon the finished article desired. The sizing solution must be of such consistency that it will adhere well to the cloth but at the same time it must not penetrate to the underside. In the case of colored oilcloths, the pattern is first printed on by engraved copper rollers, using a varnish containing a pigment. After the printing has dried a finishing coat of a long oil varnish is applied. In the case of white oilcloth the pigment is mixed with the finishing var-

<sup>112</sup> C. A. Herbst and J. D. Endriz, U. S. P. 1,932,809, Dec. 4, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 525. See Chapter 66 for discussion of technique of cold molding.

<sup>113</sup> British P. 280,178, 1928, to I. G. Farbemind. A.-G.; *Brit. Chem. Abs.* B, 1928, 444.

<sup>114</sup> G. Oeder, French P. 694,644, 1930; *Chem. Abs.*, 1931, 25, 1926. German P. 555,475, 1927; *Chem. Abs.*, 1932, 26, 5161.

<sup>115</sup> P. C. Haas, U. S. P. 1,946,790, Feb. 13, 1934; *Brit. Chem. Abs.* B, 1934, 946.

<sup>116</sup> F. R. Reumann, British P. 351,680, 1930; *Chem. Abs.*, 1932, 26, 3354. French P. 696,509, 1930; *Chem. Abs.*, 1931, 25, 2823. German P. 513,510, 1929, to Reumann-Baumasphalt G.m.b.H.; *Chem. Abs.*, 1932, 26, 278.

<sup>117</sup> G. Plauson, British P. 312,372, 1927; *Brit. Chem. Abs.* B, 1929, 633.

<sup>118</sup> German P. 593,184, 1934, to Ges. für Teerstrassenbau m.b.H.; *Chem. Abs.*, 1934, 28, 3213.

<sup>119</sup> R. A. R. Jones and J. H. P. Burke, British P. 370,917, 1930; *Brit. Chem. Abs.* B, 1932, 602.

<sup>120a</sup> F. Frits (*Chem.-Ztg.*, 1933, 57, 997; *Chem. Abs.*, 1934, 28, 2925) has discussed the preparation of linoleum and the number of substances, including cumarone resin, which may be substituted for materials (linseed oil, rosin) originally used.



nish and the printing done after the film has dried. The pigments used vary according to the product desired and, particularly the white pigments, play an important part other than merely being the coloring agent. As an illustration, zinc oxide will produce oilcloth having a high gloss while lithopone yields a coating which is not quite as glossy though tougher and more durable. In using lithopone, however, a high gloss can be obtained by special methods. One procedure is to apply a light finish coat of good quality spirit varnish. In making white oilcloth, cumarone resin has caused some difficulty in the past by yellowing.

Lender and Koch<sup>120</sup> were apparently the first to utilize cumarone resin in the manufacture of linoleum and oilcloth. The resin was added to tung oil, which had been polymerized by heating to 220-240°C., and the resulting mass was mixed with ground cork and a pigment, and pressed on a cloth backing. Better results were reported by Priest when the cumarone resin was ground with the polymerized<sup>121</sup> or oxidized<sup>122</sup> vegetable oil at a temperature of 100°C. or below. The product, so obtained, was found by Priest<sup>123</sup> to be lighter in color and to have greater adhesive properties. The elastic, gummy mass was mixed with pigment, ground cork or wood meal, and applied to the fabric by pressure. A composition of similar properties obtained by mixing one part of cumarone resin with two parts of cold tung oil gel, or by mixing one part of resin with two parts of cold oxidized linseed oil, is incorporated with the other ingredients in the following proportions: Oil-cumarone resin composition, 50 parts; pigment, 20 parts; ground cork or wood meal, 50 parts.

A binding medium for cork and wood flour in the manufacture of linoleum was prepared by Baldwin<sup>124</sup> from a mixture of 50 parts of ester gum, 50 parts of cumarone resin, 35 parts of dibutyl tartrate, and 10 parts of polymerized linseed oil. To 40 parts of this molten binder, 10 to 40 parts of wood flour, cork dust, etc., and 40 to 45 parts of pigments or fillers are added.

Floor coverings consisting of felt saturated with a nitrocellulose solution containing cumarone resin have been described by Taylor.<sup>125</sup> For example, the coating solution may have the following composition: 12 parts by weight of nitro cotton, 88 parts by weight of a solvent mixture containing as high as 35 per cent of acetone oil diluted with 65 per cent of solvent naphtha. To this mixture there may be added 12 parts of linseed oil and 12 parts of cumarone resin.

#### FLOORING AND FLOOR TILE

One of the important developments in the use of cumarone resin has been its application in the manufacture of mastic flooring and floor tile.<sup>126</sup> These compositions were originally made with asphaltic binders, blended with a solvent, pigment and fillers. The demand for lighter colored flooring necessitated substitution of a binder with lower tinting power. Cumarone resin was found to be well suited for this purpose. Resistance to washing (due to its unsaponifiable nature) as well as its color proved to be decided advantages.

A hard, pale resin is ordinarily selected and plasticized with oils and pitches of such properties that a light-colored binder is secured. This is used to the extent of about 30 per cent with asbestos fiber, slate flour, powdered silica or

<sup>120</sup> R. Lender and A. Koch, U. S. P. 1,019,666, Mar. 5, 1912; *Chem. Abs.*, 1912, 6, 1377.

<sup>121</sup> G. W. Priest, U. S. P. 1,334,049, Mar. 16, 1920, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1920, 14, 1450.

<sup>122</sup> G. W. Priest, U. S. P. 1,334,050, Mar. 16, 1920, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1920, 14, 1450.

<sup>123</sup> G. W. Priest, U. S. P. 1,381,737 and 1,381,738, June 14, 1921, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1921, 15, 3560.

<sup>124</sup> J. T. Baldwin, U. S. P. 1,793,667, Feb. 24, 1931, to Sandura Co.; *Chem. Abs.*, 1931, 25, 2314.

<sup>125</sup> C. M. Taylor, U. S. P. 1,562,383, Nov. 17, 1925; *Chem. Abs.*, 1926, 20, 272.

<sup>126</sup> J. A. Kenney, *Plastic Products*, 1934, 11 (2), 61.

whiting, as well as the proper pigments. The mixture is masticated on hot rolls or in heated Banbury mixers. The plastic mass, while still hot, is sheeted out on rolls, polished and cut into squares. Mottled, grained or marbled effects are obtained by mingling pieces of contrasting color before rolling out into flat plates.

Mastic flooring is prepared in a similar fashion, the presence of a solvent providing a more workable mass, which is applied by means of a trowel. The coating must then stand one or two days to dry and harden.

Satisfactory quality in both types of flooring depends on the skill and care of the manufacturer, particularly in regard to selection of materials. The amount of cumarone resin required may vary with the color desired. For medium light colors, bitumen may be incorporated with the cumarone resin binder, or a darker shade of the latter can be used. Asphalt alone, however, is only recommended for darker colors.

Polymerized tung oil was added to the cumarone resin binder by Bonney and Maguire<sup>127</sup> to produce a more resilient and lustrous mastic tile. For example, the following proportions were used:

Cumarone resin (3 parts) . . . . .	} 25 per cent
Tung oil (1 part) . . . . .	
Asbestos fiber . . . . .	
Pigments and mineral fillers . . . . .	
	30 per cent
	45 per cent

The oil was heated to 260-270°C. and 15 per cent of the resin added to cool it to about 230°C. The temperature was again raised to 260-270°C., after which heating was stopped and the oil allowed to polymerize. An oil-resin gel was formed and after some cooling was kneaded in a heated mixer with the fiber, fillers and the balance of the resin. The hot composition was rolled into sheets and cut to size.

#### FELT AND CLOTH SIZING

A composition for impregnating roofing felt which, at elevated temperatures, is more fluid than asphalt alone, consists of 60 to 98 per cent of asphalt of melting point not less than 32°C., together with 40 to 2 per cent of cumarone resin.<sup>128</sup>

Perry<sup>129</sup> prepared roofing felts by impregnating the watery pulp of beaten rags with an emulsion of cumarone resin and a saponified resin. The pulp was then dried in a continuous sheet by means of rolls but was not calendered as heavily as in the manufacture of paper. A similar emulsion for use in the waterproofing of fabrics was obtained by Roether<sup>130</sup> by adding paraffin, cumarone resin and linseed oil to an agitated and boiling solution of saponified coconut oil and tallow. Cloth was waterproofed by immersion in the warm liquid with subsequent wringing and calendering.

Eichler<sup>131</sup> produced a waterproof fabric or paper by impregnating the material with a cumarone resin varnish thinned to the desired consistency. It is stated that cloth woven from fibers which carry minute particles of cumarone resin may be advantageously used in lining shoes.<sup>132</sup> McCoy<sup>133</sup> used chlorinated cumarone com-

<sup>127</sup> R. D. Bonney and J. F. Maguire, U. S. P. 1,985,201, Dec. 18, 1934, to Congoleum-Nairn, Inc.; *Chem. Abs.*, 1935, 29, 1271.

<sup>128</sup> C. R. Eakert, U. S. P. 1,849,867, Mar. 15, 1932, to Barrett Co.; *Chem. Abs.*, 1932, 26, 2844

<sup>129</sup> R. P. Perry, U. S. P. 1,302,209, Apr. 29, 1919; *Chem. Abs.*, 1919, 13, 1916

<sup>130</sup> J. R. Roether, U. S. P. 1,414,670, May 2, 1922; *Chem. Abs.*, 1922, 16, 2231

<sup>131</sup> A. Eichler, U. S. P. 1,218,599, Mar. 6, 1917; *Chem. Abs.*, 1917, 11, 1757.

<sup>132</sup> H. Kahlmeyer, U. S. P. 1,931,612, Oct. 24, 1933, to United Shoe Machinery Corp.; *Chem. Abs.*, 1934, 28, 660.

<sup>133</sup> J. P. McCoy, U. S. P. 1,245,363, Nov. 6, 1918, to Westinghouse Electric & Mfg. Co.; *Chem. Abs.*, 1918, 12, 280.

pounds for treating cloth, paper, and the like, to render the material suitable for use as electrical insulation. Shaffer<sup>134</sup> utilized a solution consisting of 1 part cumarone resin, 2 parts rubber, 2 parts paraffin and 20 parts of a hydrocarbon solvent for waterproofing leather and fabrics.

#### PAPER SIZE

Although cumarone resin has been employed in the preparation of sizing for paper,<sup>135</sup> it has not readily lent itself to this purpose because of its unsaponifiable nature. Ellis,<sup>136</sup> however, found that unsaponifiable resins could be utilized by blending them with a saponifiable resin (e.g., rosin) and then emulsifying with aqueous alkali. The emulsified mixture is added to the pulp from which the paper is to be prepared and calendered in the usual manner.<sup>137</sup> Muth<sup>138</sup> also melted rosin (or fatty material) with cumarone and afterwards boiled the mixture with sufficient alkali or ammonia to give a uniform emulsion. Alkali salts of sulphonated aromatic or naphthenic acids facilitated the latter operation.<sup>139</sup> The resulting emulsion is used for sizing paper or other fibrous material. Emulsifiable resins were produced by Ellms<sup>140</sup> through careful control of the washing treatment during the manufacture of cumarone resins so that the latter contain 0.3 to 1.9 per cent of total ash of which a large proportion should be sulphonate ash. The correct amounts of ash are also attained by blending the resin with paracumarone sludges or soaps from the first alkali wash. Strobel and Tallman<sup>141</sup> prepared emulsions for sizing paper by the use of a dispersing agent consisting of abietic acid or a fatty acid cooked with 10 per cent of its weight of sodium carbonate. One procedure consists in heating mixtures of cumarone resin, asphalt, copal or gilsomite with a drying oil and the emulsifying agent at about 260°C., and adding water while the mixture is still hot. Alum is used as the precipitant.

#### PRINTING INKS

Cumarone resin has been suggested as an ingredient to replace fossil gums in printing inks. Because of its neutral character it exerts no deleterious effect on color materials. It is reported that the resin, especially in admixture with lithographic varnishes, is used in making certain types of highly satisfactory printing inks.<sup>142</sup> Other advantages, such as improvement in the luster of the printed matter and an increase in the stability of color of the ink, are partly offset by price considerations.<sup>143</sup>

McElroy and Clarke<sup>144</sup> proposed to utilize as a printing ink vehicle a solution of cumarone resin in a neutral volatile solvent, such as terpeneol, with or without the addition of rosin oil to render the binder more plastic when dried. For example, 2¼ parts of bronze powder are incorporated with 1 part of a vehicle consisting

<sup>134</sup> C. D. Shaffer, U. S. P. 1,441,605, Jan. 9, 1923; *Chem. Abs.*, 1923, 17, 1114

<sup>135</sup> C. W. Rivise, *Plastics*, 1929, 5 (5), 261; *Chem. Abs.*, 1929, 23, 3088. For a review of various paper sizes, see A. van der Werter, *Zellstoff u. Papier*, 1934, 14, 356; *Chem. Abs.*, 1935, 29, 339.

<sup>136</sup> Carleton Ellis, U. S. P. 1,007,681, Nov. 7, 1911, to Ellis-Foster Co.; *Chem. Abs.*, 1912, 6, 293.

<sup>137</sup> R. Lender, *British P.* 17,576, 1915, to W. P. Thompson; *Chem. Abs.*, 1917, 11, 1758.

<sup>138</sup> G. Muth, U. S. P. 1,194,866, Aug. 15, 1916, to Dr. Graf & Co.; *Chem. Abs.*, 1916, 10, 2638.

<sup>139</sup> German P. 345,593, 1914; *J.S.C.I.*, 1922, 41, 685A.

<sup>140</sup> German P. 348,063, 1918, to Rütgerswerke A.-G.; *J.S.C.I.*, 1922, 41, 382A.

<sup>141</sup> E. H. Ellms, U. S. P. 1,797,260, Mar. 24, 1931, to Barrett Co.; *Chem. Abs.*, 1931, 25, 2866

<sup>142</sup> C. J. Strobel and A. P. Tallman, U. S. P. 1,803,816, May 5, 1931; *Chem. Abs.*, 1931, 25, 3838.

<sup>143</sup> J. Marcusson, *Chem.-Ztg.*, 1919, 43, 93, 109, 122; *Chem. Abs.*, 1919, 13, 2607.

<sup>144</sup> E. Fonrobert, *Farben-Ztg.*, 1931, 36, 1383; *Brit. Chem. Abs. B.* 1931, 642.

<sup>145</sup> W. J. McElroy and J. Clarke, U. S. P. 1,450,692, Apr. 3, 1923; *Chem. Abs.*, 1923, 17, 1896. U. S. P. 1,471,746, Oct. 23, 1923, to Alchemio Gold Co.; *Chem. Abs.*, 1924, 18, 175. *British P.* 198,308, 1923; *J.S.C.I.*, 1923, 42, 731A.

of 16 per cent cumarone resin dissolved in 79.8 per cent of terpineol and 4.2 per cent of rosin oil to make an ink of pasty or semi-fluid consistency. Other softening agents which may be incorporated with the resin to give a non-drying ink are dibutyl phthalate, butyl stearate, diamyl phthalate and triphenyl or tricresyl phosphate.<sup>145</sup>

A composition for transferring designs from a film on a paper base to silk, leather and paper is described by Poschel.<sup>146</sup> With alcohol as the transferring liquid, the following ingredients are used: dye, Carbitol, methyl alcohol, cumarone, blown castor oil, shellac, ethylene dichloride and Cellosolve. For lithographic printing an oil- or alcohol-soluble dye is mixed with a varnish comprising chlorinated biphenyl, cumarone resin, blown castor oil, elemi resin and elemi oil. Marston and Lawrence<sup>147</sup> obtained a transfer ink by adding boiled linseed oil, mineral oil, a drier and coloring matter to molten cumarone resin melting at 95-130°C. A marking composition includes ozokerite, blown vegetable oil and cumarone resin.<sup>148</sup>

An indelible medium for conveying designs from paper to textile fabrics consists of cumarone resin and an indelible printers' ink fused together to yield a homogeneous mass.<sup>149</sup> Another formula calls for 16 parts of cumarone resin, 4 parts of rosin, 4 parts of carnauba wax, 2 parts of doubly-pressed stearic acid, 8 parts of ultramarine blue, and 40 parts of a special white ink. The latter includes 78 per cent of Titanox (titanium dioxide and precipitated barium sulphate) and 22 per cent of litho varnish, ground to a paste.<sup>150</sup> A solid, fusible transfer material was prepared by Lawrence<sup>151</sup> from a paper base and a composition containing cumarone resin, ethyl- or benzylcellulose and various solvents, oxidized oils, and coloring materials.

#### MISCELLANEOUS USES

A number of miscellaneous applications of cumarone resin have been described indicating possible methods of utilization in electrical insulation, photography and tanning of leather. For example, the resin may be dissolved in oils, particularly those of the hydrocarbon class, to increase their viscosity for the impregnation of paper insulation of cables.<sup>152</sup> The addition of polymerized cumarone and indene is also said to improve lubricating oils as regards viscosity, pour point and stability.<sup>153</sup>

Cumarone resin has been proposed by Renner and Moeller<sup>154</sup> for use in the preparation of tanning liquors. By condensing and sulphonating the resin mixed with phenols, and then oxidizing the product to quinone-like compounds, a tanning agent was obtained.<sup>155</sup>

Cumarone resin mixed with hard rubber dust yields a moldable ebonite composition,<sup>156</sup> with phthalic anhydride, glycerol and linseed oil fatty acid furnishes

<sup>145</sup> A. Schneider, U. S. P. 1,902,016, Feb. 19, 1935; *Chem. Abs.*, 1935, 29, 2375.

<sup>146</sup> A. B. Poschel, British P. 393,132, 1933; *Chem. Abs.*, 1933, 27, 5553.

<sup>147</sup> T. Marston and W. S. Lawrence, U. S. P. 1,511,816, Oct. 14, 1924, to Kaumagraph Co.; *Chem. Abs.*, 1925, 19, 185.

<sup>148</sup> W. S. Lawrence, U. S. P. 1,954,450 and 1,954,451, Apr. 10, 1934; *Brit. Chem. Abs. B*, 1935, 110 See Chapter 19.

<sup>149</sup> H. S. Sadtler, U. S. P. 1,542,965, June 23, 1925; *Chem. Abs.*, 1925, 19, 2419.

<sup>150</sup> O. L. Davis, U. S. P. 1,638,117, Oct. 14, 1928, to Joseph Walker Co.; *Chem. Abs.*, 1929, 23, 249.

<sup>151</sup> W. S. Lawrence, U. S. P. 1,899,420, Feb. 28, 1933, to Kaumagraph Co.; *Chem. Abs.*, 1933, 27, 3048.

<sup>152</sup> British P. 303,852, 1928, to Cablon, Ltd. and Dussek Bros. & Co., Ltd.; *Chem. Abs.*, 1929, 23, 4567.

<sup>153</sup> C. Wulff, F. Moll and W. Breuers, German P. 557,306, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 410 British P. 379,717, 1931; *Brit. Chem. Abs. B*, 1932, 971. French P. 718,516, 1931; *Chem. Abs.*, 1932, 26, 8102.

<sup>154</sup> H. Renner and W. Moeller, British P. 148,750, 1920; *J.S.C.I.*, 1922, 41, 185A.

<sup>155</sup> H. M. Bunbury and A. Davidson, *Chem. Age* (London), 1925, 13, 298.

<sup>156</sup> H. Gray, U. S. P. 1,769,506, Jan. 7, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 4666.

a molding and coating composition,<sup>157</sup> and with phenol-formaldehyde resin and Portland cement gives an adhesive for linoleum.<sup>158</sup>

Molten cumarone resin has been employed as a medium for curing molded products under hydrostatic pressure. In this case, the procedure calls for partial curing of the article in a mechanical mold followed by immersion in the molten resin for the final curing under pressure.<sup>159</sup> Less than 5 per cent of the resin is used to fix a depolarizing mass to salt-containing carbon elements in electric batteries.<sup>160</sup> An arc-welding electrode recommended by Notvest<sup>161</sup> consists essentially of a ferrous rod coated with a fluxing material containing cumarone resin.

Other uses suggested for cumarone resin are as an ingredient in light-sensitive varnishes for photographic media,<sup>162</sup> as a preservative coating for coffee beans,<sup>163</sup> and in the preparation of rust removers.<sup>164</sup> A representative composition of the latter type consists of 1 part of resin, 5 parts of xylene and 3 parts of sperm oil.

<sup>157</sup> C. G. Moore and M. Zucker, U. S. P. 1,915,544, June 27, 1933, to Glidden Co.; *Chem. Abs.*, 1933, 27, 4431. Another molding composition consists of an alkyl resin dissolved in indene: L. V. Adams, U. S. P. 1,849,817, Mar. 15, 1932, to General Elec. Co.; *Brit. Chem. Abs. B*, 1933, 78. See also British P. 381,693, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 158.

<sup>158</sup> R. D. Bonney and A. G. de Boer, U. S. P. 1,901,007, Feb. 12, 1935, to Congoleum-Naun, Inc.; *Chem. Abs.*, 1935, 29, 2262.

<sup>159</sup> F. S. Smith, U. S. P. 1,627,209, May 3, 1927, to Products Protection Corp.; *Chem. Abs.*, 1927, 21, 2174.

<sup>160</sup> A. Kunze, British P. 332,155, 1929; *Brit. Chem. Abs. B*, 1930, 869.

<sup>161</sup> R. Notvest, U. S. P. 1,931,466, Oct. 17, 1933, to J. D. Adams Mfg. Co.; *Chem. Abs.*, 1934, 28, 94.

<sup>162</sup> British P. 270,386, 1926 and 270,387, 1926, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1928, 22, 1552.

<sup>163</sup> J. Bordas, *Ann. fals.*, 1923, 16, 221; *Chem. Abs.*, 1923, 17, 2756.

<sup>164</sup> C. M. Abbott, U. S. P. 1,333,363, Mar. 9, 1920, to Polygon Products Co.; *Chem. Abs.*, 1920, 14, 1419.

## Chapter 8

### Resins from Acetylene

The possibilities of acetylene as a raw material for the production of high grade resinous or resin-forming substances have only been realized during the last few years. Acetylene is a cheap and abundant raw material and, at the present time, its conversion to synthetic rubber-like substances, drying oils and similar products is being actively exploited by at least one large company in the United States. Although the principal source of acetylene at present is calcium carbide, considerable quantities are being manufactured by the action of an electric arc on both natural gas and the gases from petroleum cracking.<sup>1</sup>

The conversion of acetylene into high-molecular-weight, amorphous materials takes place by a process of additive polymerization. However, valuable synthetic products of this type are now being made by the action of various chemical reagents, including hydrogen chloride, hydrogen bromide and sulphur chloride, on the lower polymers of acetylene. Accordingly, it becomes necessary to consider the polymerization reactions of acetylene with particular reference to the production of high-molecular-weight, resinous and amorphous polymers and also of its lower highly unstable ones, which can themselves be converted into such amorphous substances.

#### POLYMERIZATION OF ACETYLENE

Acetylene may be polymerized by a large number of agents.<sup>2</sup> Among these may be mentioned heat, light, electricity and various chemical substances.

The thermal polymerization of acetylene at temperatures above about 400°C. has been studied by a large number of investigators.<sup>3</sup> At these elevated temperatures both in the absence and also in the presence of solid contact materials, condensation to liquid and tarry substances takes place readily. These polymers are mainly of an aromatic character and a large number of mononuclear and polynuclear aromatic hydrocarbons have been identified in the liquid products of the reaction. From the point of view of the formation of resinous bodies, the high temperature treatment of acetylene would appear to be of no practical importance.

As might be expected, the presence of certain catalysts causes acetylene to undergo condensation at comparatively low temperatures with the formation of products of a nature essentially different from those formed at higher tempera-

<sup>1</sup> For a discussion of the action of an electric arc on hydrocarbons see Carleton Ellis, "Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934, Chapter 9.

<sup>2</sup> G. Egloff, C. D. Lowry, Jr., and R. E. Schand, *J. Phys. Chem.*, 1932, 36, 1457-1520; *Chem. Abs.*, 1932, 26, 3479.

<sup>3</sup> M. Berthelot, *Compt. rend.*, 1866, 63, 479, 515. R. Meyer and co-workers, *Ber.*, 1912, 45, 1609, 1914, 47, 2765; 1918, 51, 1571; 1920, 53, 1261. *Chem. Abs.*, 1912, 6, 2618; 1915, 9, 306; 1919, 13, 1324, 1920, 14, 3669. N. Zelinskij, *Ber.*, 1924, 57, 264; *Chem. Abs.*, 1924, 18, 2125; *Compt. rend.*, 1923, 177, 882; *Chem. Abs.*, 1924, 18, 656. A. Krovache and E. Turot, *Chim. et ind.*, 1925, 13, 301, 537; *Chem. Abs.*, 1925, 19, 2035. F. Fischer, F. Bangert and H. Pichler, *Brennstoff-Chem.*, 1929, 10, 279; *Chem. Abs.*, 1930, 24, 483. E. Berl and K. W. Hofmann, *Z. anorg. Chem.*, 1931, 44, 259; *Chem. Abs.*, 1931, 25, 3309. C. Fujio, *J. Soc. Chem. Ind. Japan*, 1928, 31, 77; *Chem. Abs.*, 1928, 22, 2363. R. N. Pease, *J. A. C. S.*, 1929, 51, 3470.

tures. Of the greatest importance is the extraordinary activity of metallic copper, which catalyzes the condensation of acetylene to a high-molecular-weight, amorphous substance at temperatures above about 180°C. The formation of this polymer, to which the name "Cuprene" has been assigned, is discussed fully at a later stage. Small amounts of cuprene-like materials are also produced from acetylene in the presence of metallic iron, nickel and cobalt at temperatures ranging from room temperature to about 400°C. but the main products of reaction in these cases consist of carbon, hydrogen and some oily substances.

Gambarjan<sup>4</sup> investigated the formation of a cuprene-like substance prepared by the reaction of bromine on a suspension of aluminum in chloroform. He found the essential reaction to be that of bromoform on aluminum probably yielding acetylene. This in turn reacted to form the solid in question.

The action of the silent electric discharge on acetylene gas, a subject investigated by a number of workers, gives rise to solid, insoluble and amorphous polymerization products as well as unstable liquids and gases. Among the gases are hydrogen and methane. Berthelot<sup>5</sup> observed that acetylene was converted, under the influence of the silent discharge into a thick, brown liquid, a brown solid and a small amount of gas. A semisolid, brown substance obtained by Jackson and Northall-Laurie<sup>6</sup> through subjecting acetylene to a high-frequency discharge was found by analysis to be a true polymer of acetylene, but it rapidly absorbed up to 8 per cent of oxygen when exposed to the air and was converted into an insoluble, hard solid. Losanitsch<sup>7</sup> reported that the silent electric discharge transformed acetylene into a thick, brown liquid, which later changed to a solid mass. The product could be separated by the use of an alcohol-ether mixture into a soluble, viscous substance and an insoluble solid. These materials rapidly absorbed oxygen on exposure to air.<sup>8</sup> Much light was thrown on the character of these polymers by Kaufmann<sup>9</sup> who obtained a viscous, brown liquid together with a brittle, pale yellow solid by passing a stream of acetylene through a silent discharge tube. The liquid product, which was formed exclusively when the reaction vessel was cooled, was rapidly polymerized to an insoluble solid on warming and on distillation left a plastic or brittle residue. The liquid rapidly absorbed oxygen and also formed an explosive silver derivative, implying the presence of acetylenic hydrocarbons. The solid formed in the discharge tube was a pale yellow, odorless powder insoluble in all solvents. Kaufmann considered this substance to be essentially aliphatic in nature as contrasted with cuprene which is thought by some investigators to be a polynuclear, aromatic material.

The lower, liquid polymers of acetylene have been obtained by Mignonac and de Saint-Aunay<sup>10</sup> through exposing the gas to a high-frequency discharge and cooling the electrodes to -60°C. The liquid, whose molecular weight determination indicated it to be composed of trimers of acetylene, was a mixture of several hydrocarbons and contained about 40 per cent of diacetylenes and no monoacetylenes. Its empirical formula has been calculated to be approximately  $(C_{10}H_8)_n$ .<sup>11</sup> Reduction of this mixture of trimers yielded hexane and, from the products of oxidation, the presence of dipropargyl,  $HC\equiv C-CH_2-CH_2-C\equiv CH$ , 3-methyl-1,4-pen-

<sup>4</sup> S. Gambarjan, *Ber.*, 1928, 61, 177; *Chem. Abs.*, 1928, 22, 1324.

<sup>5</sup> M. Berthelot, *Compt. rend.*, 1890, 111, 471; 1898, 126, 570; *J.C.S.*, 1891, 60, 28; 1898, 74 (1) 393 *Ann. chim. phys.*, 1877, (5) 10, 67; 1891, (6) 24, 135; *Chem. Zentr.*, 1877, 178, 1891, 2, 577.

<sup>6</sup> H. Jackson and D. Northall-Laurie, *Proc. Chem. Soc.*, 1906, 22, 155; *Chem. Zentr.*, 1906, 2, 858. See also P. Schutzenberger, *Compt. rend.*, 1890, 110, 889, *J.C.S.*, 1890, 58, 961.

<sup>7</sup> S. M. Losanitsch, *Ber.*, 1907, 40, 4656; *Chem. Abs.*, 1908, 2, 760; *Bull. sci. acad. roy. Belge*, 1925, (5) 11, 324; see also M. Z. Yovitchitch, *Monatsh.*, 1908, 29, 5; *Chem. Abs.*, 1908, 2, 1418.

<sup>8</sup> M. Z. Yovitchitch, *Bull. sci. acad. roy. Belge*, 1924, (5) 10, 465; 1927, (5) 13, 365; *Chem. Abs.*, 1925, 19, 2298; 1928, 22, 2114.

<sup>9</sup> H. P. Kaufmann, *Ann.*, 1918, 417, 34; *Chem. Abs.*, 1919, 13, 1825.

<sup>10</sup> G. Mignonac and R. V. de Saint-Aunay, *Compt. rend.*, 1929, 188, 959, *Chem. Abs.*, 1929, 23, 3437 R. V. de Saint-Aunay, *Chim. et Ind.*, 1933, 29, 1011; *Chem. Abs.*, 1933, 27, 3911.

<sup>11</sup> S. C. Lind and R. Livingston, *J.A.C.S.*, 1934, 56, 1550.

tadiyne,  $\text{HC}\equiv\text{C}-\text{CH}(\text{CH}_3)-\text{C}\equiv\text{CH}$ , and 1,5-hexadiene-3-yne,  $\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$ , was inferred. The trimeric material slowly underwent polymerization to a brown resin.

When acetylene is exposed to light of wave length shorter than 2500-3000Å, it undergoes polymerization even at low temperatures with the formation of a yellowish-brown, amorphous solid, insoluble in most solvents. This material appears to be similar to cuprene.<sup>12</sup> Exposure of a saturated aqueous solution of acetylene to the light of a mercury arc yields a white, inert, insoluble polymer.<sup>13</sup> Benzene and anthracene derivatives have also been detected.<sup>14</sup> Mercury vapor exerts a catalytic effect on the polymerization of acetylene in ultraviolet light, according to Toul.<sup>15</sup>

Under the influence of alpha-radiation acetylene undergoes condensation with the formation of a voluminous, brownish-yellow, amorphous powder. Mund and Koch<sup>16</sup> found that this material did not melt at 300°C. but did not investigate its chemical nature. Lind and Bardwell<sup>17</sup> likewise obtained a yellowish powder, similar to cuprene, on exposure of acetylene to radium emanation. Lind, Jungers and Shifflett<sup>18</sup> observed that acetylene and heavy acetylene (from calcium carbide and heavy water) polymerized at equal velocities to solid cuprenes on exposure to γ-rays from radon.

The production of a yellow, amorphous, cuprene-like material from acetylene has also been observed to take place under the influence of cathode rays.<sup>19</sup> According to Marshall,<sup>20</sup> polymerization to a fluffy, yellow powder is the only reaction occurring under these circumstances, no elimination of hydrogen being noticed. When acetylene was heated during irradiation the yield of solid was not changed but the powder increased in density and assumed a darker color. On exposure to air, Marshall found that this polymer could absorb as much as 30 per cent of its weight of oxygen.

Moens and Juliard<sup>21</sup> noted that acetylene was rapidly converted into a yellowish-white powder when subjected to the action of a high-frequency electro-magnetic field.

#### THE POLYMERIZATION OF ACETYLENE TO CUPRENE

Cuprene,<sup>22</sup> or carbene, is a voluminous, yellowish-brown solid obtained by the condensation of acetylene in the presence of copper or alloys of copper at temperatures usually above 180°C. The production of this material by the action of acetylene at 230°C. on cuprous oxide, or more slowly in the presence of finely divided copper, was first reported by Erdmann and Köthner.<sup>23</sup> Passage of acetylene for 18 hours over one g. of cuprous oxide furnishes 7 g. of cuprene having an

<sup>12</sup> S. C. Lind and R. S. Livingston, *J.A.C.S.*, 1930, 52, 6413; 1932, 54, 94; H. Remicke, *Z. angew. Chem.*, 1928, 41, 1144; *Chem. Abs.*, 1929, 23, 1352. See also D. Berthelot and H. Gaudechon, *Compt. rend.*, 1910, 150, 1169; 1912, 155, 207; *Chem. Abs.*, 1910, 4, 2097; 1912, 6, 3049.

<sup>13</sup> R. Livingston and C. H. Shifflett, *J. Phys. Chem.*, 1932, 36, 750; *Chem. Abs.*, 1932, 26, 2118.  
<sup>14</sup> W. Kemula and S. Mrazek, *Z. phys. Chem.*, 1933, 23B, 358; *Brit. Chem. Abs. A*, 1934, 168.  
R. Livingston and C. H. Shifflett, *J. Phys. Chem.*, 1934, 38, 377; *Chem. Abs.*, 1934, 28, 3663.

<sup>15</sup> F. Toul, *Coll. Czech. Chem. Comm.*, 1934, 6, 162; *Brit. Chem. Abs. A*, 1934, 852.

<sup>16</sup> W. Mund and W. Koch, *Bull. soc. chim. Belge*, 1925, 34, 119; *Chem. Abs.*, 1925, 19, 1986.  
<sup>17</sup> S. C. Lind and D. C. Bardwell, *Science*, 1925, 62, 422, 593; 1926, 63, 310; *Chem. Abs.*, 1926, 20, 1031, 702, 1760. S. C. Lind, D. C. Bardwell and J. H. Perry, *J.A.C.S.*, 1931, 48, 1556.

<sup>18</sup> S. C. Lind, J. C. Jungers and C. H. Shifflett, *Phys. Rev.*, 1934, 46, 825; *Chem. Abs.*, 1935, 29, 51.  
<sup>19</sup> W. D. Coolidge, *Science*, 1925, 62, 441; *Chem. Abs.*, 1926, 20, 2615. J. C. McLennan, M. W. Perrin and H. J. C. Ireton, *Proc. Roy. Soc.*, 1929, 125A, 246; *Chem. Abs.*, 1930, 24, 23.

<sup>20</sup> See G. Egloff, C. D. Lowry, Jr., and R. E. Schaad, *loc. cit.*

<sup>21</sup> R. Moens and A. Juliard, *Bull. acad. roy. Belge*, 1927 (5) 13, 201; *Brit. Chem. Abs. A*, 1927, 1042.  
<sup>22</sup> Reviews, dealing with cuprene, have been contributed by W. Herzog, *Chem.-Ztg.*, 1931, 55, 461, 478; *Brit. Chem. Abs. B*, 1931, 796. *Kunststoffe*, 1931, 21, 49; *Chem. Abs.*, 1931, 25, 2683. *Osterr. Chem.-Ztg.*, 1927, 30, 73; *Chem. Abs.*, 1927, 21, 2870. Also, A. Poulon, *Z. ges. Schuess-Sprengstoffw.*, 1932, 27, 48; *Chem. Abs.*, 1932, 26, 2596.

<sup>23</sup> H. Erdmann and P. Köthner, *Z. anorg. Chem.*, 1898, 18, 49, 57; *J.C.S.*, 1899, 76 (1), 21.



apparent volume of no less than 300 cc. The material was at first considered by Erdmann and Köthner to be a complex, nonexplosive copper acetylide of the formula,  $C_6H_2Cu_3$ , but was shown later by Gooch and Baldwin<sup>24</sup> to consist of a mixture of copper or its oxide with a complex hydrocarbon. The experiments of these investigators showed further that, although metallic copper may induce polymerization of acetylene at comparatively high temperatures, the formation of cuprene is started at moderately low temperatures by an oxidizing action. The important role of oxygen in this process was subsequently confirmed by Kaufmann and his co-workers.

Sabatier and Senderens<sup>25</sup> found that reduced copper induced the polymerization of acetylene at 180-250°C. to a yellowish-brown mass. This material consisted of a substance of the empirical formula,  $(C_7H_8)_n$ , (to which the name "cuprene" was applied) mixed with about 1.5 per cent copper. In addition to cuprene, a greenish tar and also small amounts of saturated and unsaturated hydrocarbons were obtained. Sabatier and Senderens suggested that cuprene resulted from the interaction of an intermediate acetylide with fresh acetylene.

Valuable information regarding the mechanism of the formation of cuprene has been supplied by Kaufmann and Schneider.<sup>26</sup> Comparative experiments on the condensation of acetylene in the presence of reduced copper, cuprous oxide, cupric oxide and a residue obtained by heating anhydrous copper ferrocyanide in a current of air at 250°C. for 15 minutes showed that the last catalyst gave the best yields of cuprene. The physical character of the substance was altered by the catalyst employed and the duration of heating. Its empirical composition also varied between  $(C_{11}H_{10})_x$  and  $(C_{16}H_{10})_x$ . With short periods of heating, the product was loose and voluminous, but, on continued exposure to the reaction temperature, a cork-like body was obtained. The material made in the presence of the copper-ferrocyanide catalyst was yellow to light brown whereas the other catalysts furnished much darker products. Subsequent experiments of Kaufmann and Mohnhaupt<sup>27</sup> showed that the conversion of very pure acetylene to cuprene in the presence of fully reduced copper at 230-300°C. did not take place unless small amounts of oxygen were present. It was believed by these investigators that cuprene resulted from the formation of an additive compound of acetylene and cuprous or cupric oxide. Decomposition of this double compound was considered to furnish a highly active form of acetylene capable of undergoing profound reactions more rapidly than the ordinary inactive form, while the regenerated copper oxide could then activate more acetylene. Unlike the compounds obtained by the polymerization of acetylene under the influence of the silent discharge, alpha-radiation or actinic light, cuprene did not absorb oxygen in the cold. It was halogenated only with difficulty and was oxidized to mellitic acid by nitric acid. These facts led Kaufmann and Mohnhaupt to assign a polynuclear aromatic structure to cuprene.

According to Schläpfer and Stadler,<sup>28</sup> cuprene has been prepared by the Elektrizitätswerk Lonza A.-G. Passage of technical acetylene, diluted with an inert gas, over finely divided copper heated to 300°C. yielded 75-80 per cent of cuprene, 5.5-7 per cent of cuprene tar and 13-17 per cent of waste gases. A detailed examination of the tar by the above investigators showed that it consisted mainly of

<sup>24</sup> F. A. Gooch and De Forest Baldwin, *Z. anorg. Chem.*, 1899, 22, 235; *J.C.S.*, 1900, 78 (1), 74. See also H. Alexander, *Ber.*, 1899, 32, 2381; *J.C.S.*, 1899, 76, (1), 843.

<sup>25</sup> P. Sabatier and J. B. Senderens, *Compt. rend.*, 1900, 130, 250; *J.C.S.*, 1900, 78 (1), 197. *Bull. soc. chim.*, 1899, (3) 21, 530; *J.S.C.I.*, 1900, 19, 230. *Ann. chim. phys.*, 1905, (8) 4, 439. *J.C.S.*, 1905, 88, (1), 401. See also *Compt. rend.*, 1899, 128, 1173; *J.C.S.*, 1899, 76, (1), 555.

<sup>26</sup> H. P. Kaufmann and M. Schneider, *Ber.*, 1922, 55, 267; *Chem. Abs.*, 1922, 16, 2302.

<sup>27</sup> H. P. Kaufmann and W. Mohnhaupt, *Ber.*, 1923, 56, 2533; *Chem. Abs.*, 1924, 18, 1465. *J.C.S.*, 1924, 126 (1), 130.

<sup>28</sup> P. Schläpfer and O. Stadler, *Helv. Chim. Acta*, 1926, 9, 185; *Chem. Abs.*, 1926, 20, 1384.

aromatic hydrocarbons of the benzene and naphthalene series. Smaller quantities of olefins (hexenes and octenes) and small amounts of paraffin hydrocarbons boiling between 28-64°C. under 720 mm. were also present. The technical details of the manufacture of cuprene have so far remained a secret. It is known definitely, however, that the presence of oxygen (air) is a necessary factor and that copper or cupriferous bronze powders are used as catalysts at a temperature of 200-260°C. under slight pressure and with the combined action of dark electric discharges.<sup>30</sup> The addition of air, oxygen or an oxygen-supplying agent to the acetylene prior to condensation in order to increase the yield of cuprene has been described by Horwitz.<sup>30</sup> Lichtenhahn<sup>31</sup> prevented choking of the reaction tube by the use of a special stirring mechanism. Addition of 5-15 per cent of nitrogen to acetylene minimizes coking (which is very pronounced with pure acetylene owing to the highly exothermic nature of the reaction) and gives a more homogeneous and lighter-colored cuprene. In another process,<sup>32</sup> cuprene was produced by passing acetylene, diluted by an inert gas, through a suspension of copper-bronze in stearic acid, or paraffin oil containing copper oleate, heated to 300°C. Cuprene obtained in this manner is finely powdered and light to dark brown in color. Addition of air or oxygen to the contact medium has been found advantageous.

In the process of de Liefde,<sup>33</sup> cuprene having strongly absorbent properties and useful as a decolorizing material is prepared by subjecting acetylene at 200-400°C. to the action of a metal or metal oxide catalyst (copper, nickel or iron or their oxides) containing a small amount, usually less than 1 per cent, of magnesium. Cuprous oxide with one per cent of stannic oxide converted acetylene to a soft, flocculent product at 180-245°C. and to a brittle, porous substance at 250-260°C., according to Davis and Levy.<sup>34</sup> Sabatier and Mailhe conducted benzyl alcohol vapors over titanium, tungsten and aluminum oxides and obtained a resinous hydrocarbon having the elementary formula,  $C_7H_6$ . The resin is insoluble and appears to be somewhat analogous to cuprene.<sup>35</sup>

#### INDUSTRIAL USES OF CUPRENE

Because of its chemical inertness and highly voluminous structure, cuprene offers possibilities for a large number of industrial applications. Herzog<sup>36</sup> has discussed its use in the manufacture of acid-resistant and electric-insulating materials, plastic masses, electrodes and explosives, as a cork substitute in linoleum manufacture and as an absorbing agent for illuminating materials, fuels and volatile substances. It can be used as a substitute for carbon in black powder and other explosives, an absorbent in liquid-air explosives, a component of detonators and a substitute for kieselguhr.

Finely ground cuprene has been used by Sulser<sup>37</sup> in conjunction with a linoleum cement for the production of linoleum. It replaced the usual cork dust or wood

<sup>30</sup> W. Herzog, *Kunststoffe*, 1931, 21, 49; *Chem. Abs.*, 1931, 25, 2683.

<sup>31</sup> L. Horwitz, German P. 205,705, 1907; *Chem. Abs.*, 1909, 3, 1925.

<sup>32</sup> T. Lichtenhahn, Canadian P. 238,838, 1924; *Chem. Abs.*, 1924, 18, 1300. British P. 200,087, 1923 to Elektrizitätswerk Lonza A.-G.; *Chem. Abs.*, 1924, 18, 276. Swiss P. 95,237, 1921. German P. 395,549, 1922.

<sup>33</sup> German P. 407,485, 1922, to Elektrizitätswerk Lonza A.-G.; *J.S.C.I.*, 1925, 44, 474B.

<sup>34</sup> W. C. de Liefde, U. S. P. 1,828,560, Oct. 20, 1931, to N.-V. Electro-Zuurstoffen, Waterstoffabriek; *Chem. Abs.*, 1932, 26, 814. British P. 303,797, 1928; *Chem. Abs.*, 1929, 23, 4485. German P. 534,118, 1929; *Chem. Abs.*, 1932, 26, 735.

<sup>35</sup> R. H. Davis and L. A. Levy, British P. 418,005, 1934; *Brit. Chem. Abs. B*, 1935, 13.

<sup>36</sup> P. Sabatier and A. Mailhe, *Ann. chim. phys.*, 1910, (8) 20, 289; *Chem. Zentr.*, 1910, 2, 1136. *Compt. rend.*, 1908, 147, 106; *Chem. Zentr.*, 1908, 2, 676.

<sup>37</sup> W. Hersog, *loc. cit.*

<sup>38</sup> J. Sulser, U. S. P. 1,511,784, Oct. 14, 1924, to Elektrizitätswerk Lonza A.-G.; *Chem. Abs.*, 1925, 19 186. British P. 189,146, 1921; *Chem. Abs.*, 1923, 17, 2482. German P. 395,706, 1921; *Kunststoffe*, 1925, 15, 122.

flour. Cuprene possesses the advantage for this purpose that it is resistant to moisture and therefore not liable to rot.

Lepsius<sup>38</sup> proposed cuprene saturated with a liquid combustible material as a fuel. Cuprene is stated to be capable of absorbing large quantities of liquid and to have a high calorific value. An elastic composition of durable character has been prepared by Kühn<sup>39</sup> by mixing cuprene with a rubber composition. Plastic masses which could be used in electrical or heat insulation have been manufactured by heating an excess of the condensation products of acetylene with sulphur and an inert material (e.g., asbestos) together with the residues from the distillation of natural resins or oils boiling above 350°C. from tar distillation.<sup>40</sup> Grimwood<sup>41</sup> suggested the substitution of cuprene for all or part of the charcoal used in time rings for shell fuses. Absorbent masses for various purposes are obtained by activating cuprene through heating it for one hour or more in hydrogen at 400-700°C.<sup>42</sup>

Sulphurized cuprene, containing 11 per cent of sulphur, can be prepared by heating cuprene with sulphur monochloride in a reflux apparatus employing benzene as suspending agent. By operating under 10 atmospheres pressure at 180-200°C., a product containing 13.6 per cent of sulphur and 4 per cent of chlorine was obtained. These materials may find application in the rubber industry.<sup>43</sup>

#### CONTROLLED POLYMERIZATION OF ACETYLENE TO LOW-BOILING, UNSATURATED POLYMERS

One development in the conversion of acetylene into resinous and rubber-like materials has resulted from a study of the controlled polymerization of that hydrocarbon at ordinary temperatures under the influence of a solution of ammonium and cuprous chlorides. Under these conditions acetylene is polymerized to a dimer and a trimer, both of which may be utilized as raw materials for the manufacture of synthetic drying oils, resins and rubber-like substances. The fundamental discovery of the conversion of acetylene into its highly unsaturated, lower polymers by controlled polymerization is due to Nieuwland and his associates. Preliminary observations of the conversion of acetylene into some other material by catalytic action of a solution of cuprous chloride and sodium or potassium chloride were made by Nieuwland as early as 1906, but it was not until 1921 that the idea of using concentrated, cuprous chloride solution occurred to him. Such concentrated, cuprous chloride solutions were attainable by the use of ammonium chloride or amine salts. Divinylacetylene, or 1,5-hexadiene-3-yne, was the first polymer to be definitely identified among the products of reaction.<sup>44</sup>

When acetylene is passed into a concentrated solution of cuprous ammonium chloride, rapid absorption takes place with the formation of a complex compound. If this complex is heated soon after its formation, acetylene is evolved practically quantitatively. After the solution is allowed to stand at room temperature for a period of 120 hours or longer, no acetylene appears in reaction products; but, instead, polymers of acetylene with molecular weights corresponding to the formulas  $C_4H_4$  and  $C_6H_6$ . The mechanism of the reaction, as envisaged by Nieuw-

<sup>38</sup> K. Lepsius, German P. 396,289, 1921; *J. S. C. I.*, 1924, 43, 818B.

<sup>39</sup> E. Kühn, U. S. P. 1,522,822, Jan. 13, 1925; *Chem. Abs.*, 1925, 19, 909. See also British P. 192,030, 1923, to Elektrizitätswerk Lonsa; *Chem. Abs.*, 1923, 17, 3429; Swiss P. 102,757, 1923; *Kunststoffe*, 1923, 15, 45.

<sup>40</sup> German P. 455,551, 1923 to Sinit A.-G.; *Brit. Chem. Abs. B.*, 1930, 157.

<sup>41</sup> A. J. Grimwood, British P. 233,741, 1927, to Curtis's & Harvey, Ltd.; *Brit. Chem. Abs. B.*, 1928, 245.

<sup>42</sup> Dutch P. 20,851, 1929, to N. V. Electro-Zuurstof en Waterstoffabriek; *Chem. Abs.*, 1930, 24, 93f.

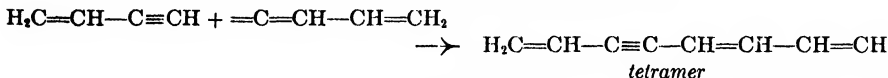
<sup>43</sup> W. Herzog, *Kunststoffe*, 1931, 21, 49; *Chem. Abs.*, 1931, 25, 2683.

<sup>44</sup> J. A. Nieuwland, *Science*, 1922, 56, 486.

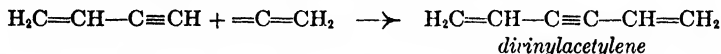
land, Calcott, Downing and Carter,<sup>46</sup> consists in the formation of a complex cuprous salt which is in equilibrium with normal acetylene and an activated form of acetylene, possibly  $\text{C}=\text{CH}_2$ . A slow combination of this activated acetylene molecule with one of normal acetylene follows, producing monovinylacetylene, butenyne, according to the scheme:



Two molecules of monovinylacetylene, in the presence of the cuprous ammonium chloride solution, unite to give a tetramer of acetylene (which is probably 1,5,7-octatriene-3-yne). The latter substance is formed by the addition of an activated vinylacetylene to a normal molecule of that compound, thus:



In the presence of acetylene, monovinylacetylene and activated acetylene may react to form divinylacetylene according to the equation,



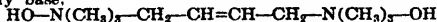
From the commercial standpoint the most valuable of these polymers of acetylene are monovinylacetylene and divinylacetylene. The latter can be obtained in good yields by a fairly simple procedure. Since monovinylacetylene so readily reacts with more acetylene, the preparation of good yields of it is more difficult.<sup>46</sup> A satisfactory laboratory method for the synthesis of divinylacetylene is as follows:<sup>47</sup>

A mixture of 1000 g. of cuprous chloride, 390 g. of ammonium chloride, 100 g. of precipitated copper powder, 30 g. of hydrochloric acid (37 per cent) and 425 g. of water is introduced into a 2 liter flask and heated on a steam bath (in the absence of air) until all the copper is in the cuprous state. The catalyst is cooled to room temperature and charged by sweeping the air from the flask with a stream of acetylene and then continuing a slight pressure of that gas while agitating the catalyst. During absorption, the latter may warm up and a temperature of 40-50°C. can be attained without damage. Over 100 g. of acetylene will be absorbed and the catalyst becomes light yellow in color as insoluble addition compounds are formed. The mixture is allowed to age at room temperature for 5-7 days and then distilled by heating in an oil bath at 100-110°C. (still temperature), until only water comes over. The lower aqueous layer of the distillate is separated and returned to the catalyst mixture for re-use.<sup>48</sup> The oily layer is dried and distilled *in vacuo* on a water-bath. Divinylacetylene comes over under about 200 mm. pressure and the tetramer under about 20 mm. The yields, based on the acetylene absorbed, are: divinylacetylene, 70-80 per cent; tetramer, 10 per cent; and loss, 10-20 per cent. Divinylacetylene, which forms explosive substances on exposure to air, is best stored in the catalytic mixture and distilled immediately prior to use.

Nieuwland<sup>49</sup> has described the production of various derivatives of acetylene containing the group,  $\text{CH}_2=\text{CH}-$ , or its tautomeric form,  $\text{CH}_2-\text{CH}=\text{X}$ , where X is an atom of carbon, nitrogen, oxygen or sulphur bound by a double bond to the ethylidene group. The preparation of two of these, divinylacetylene and the acetylene tetramer, has been described above. Ethylidene aniline and its polymers

<sup>46</sup> J. A. Nieuwland, W. S. Calcott, F. B. Downing and A. S. Carter, *J.A.C.S.*, 1931, 53, 4197.

<sup>47</sup> For laboratory preparation of monovinylacetylene, the method of R. Willstätter and T. Wirth (*Ber.*, 1913, 46, 538; *Chem. Abs.*, 1913, 7, 1508) is recommended. This procedure involves the distillation of the quaternary base,



See also E. A. Shilov, A. N. Makashina and G. I. Yakimov (*Sintet. Kautchuk*, 1933 (1), 4; *Chem. Abs.*, 1933, 27, 5052) for modifications of the procedure.

<sup>48</sup> J. A. Nieuwland, W. S. Calcott, F. B. Downing and A. S. Carter, *loc. cit.*

<sup>49</sup> The catalyst can be used repeatedly over long periods without diminution of polymerizing power.

<sup>49</sup> J. A. Nieuwland, U. S. P. 1,811,950, June 30, 1931, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, 1931, 25, 4892. *British P.* 384,654, 1932; *Chem. Abs.*, 1933, 27, 4251. *French P.* 733,663, 1931; *Chem. Abs.*, 1933, 27, 1011. *German P.* 538,283, 1933; *Chem. Abs.*, 1934, 28, 1360.

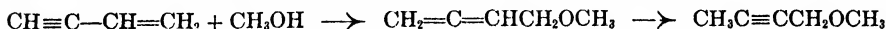
were obtained by introducing acetylene into a mixture of 2 parts of cuprous chloride powder and 100 parts of amline at 70-110°C. Vinyl chloride may be synthesized by using a mixture of ammonium and cuprous chlorides in hydrochloric acid (sp. gr. 1.194) at 20-40°.

The process has been made continuous by Calcott and Downing.<sup>60</sup> They pass the stream of acetylene rapidly in contact with the heated catalyst mixture in order to favor the formation of the dimer, vinylacetylene, over that of the trimer, divinylacetylene. Nieuwland<sup>61</sup> has improved the catalyst used by bringing the  $p_H$  to 6 or lower through incorporation of an inorganic or carboxylic acid which does not precipitate cuprous copper. In addition to these variations, the vinylacetylene may be continuously removed by a counter-current stream of mineral oil<sup>62</sup> or the reaction carried out in a non-aqueous solvent such as ethylene glycol.<sup>63</sup>

An essentially neutral solution of ammonium chlorocuprite is employed by Perkins and Toussaint<sup>64</sup> to secure a maximum yield of monovinylacetylene. The catalyst is prepared by dissolving 300 g. cuprous chloride, 300 g. ammonium chloride and 70 cc. concentrated hydrochloric acid in 600 cc. of water, heating to 90°C. and filtering. After saturating with acetylene, ammonium hydroxide is added until a black precipitate forms. This is dissolved with the minimum amount of hydrochloric acid. When acetylene is passed through at about 70°, a yield of 24 per cent vinylacetylene and 3 per cent higher boiling compounds is obtained.

#### MONOVINYLACETYLENE, $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$

This material is a colorless liquid boiling at +5°C. at 757 mm. and having the sharp but sweet odor associated with synthetic butadiene. Its density is given by the equation  $d_4^{20} = 0.7095 - 0.00114t$  for temperatures between -3° and -80°C. It congeals to a crystalline mass at the temperature of liquid air. Its structure is proved by the fact that it can be hydrogenated to n-butane and hydrated in the presence of mercuric sulphate and sulphuric acid to yield the unsaturated ketone 1-butene-3-one (methyl vinyl ketone),  $\text{CH}_2=\text{CH}-\text{CO}-\text{CH}_3$ .<sup>65</sup> The presence of acetylenic hydrogen is indicated by its ready formation of a white silver derivative and a yellow copper salt. Alcohols<sup>66</sup> combine readily with vinylacetylene to yield ethers. For example, 4-methoxy-2-butyne ( $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{OCH}_3$ ) results when methyl alcohol containing a little sodium methylate is treated with vinylacetylene. In this instance addition of alcohol to the unsaturated hydrocarbon probably takes place at the 1,4 positions followed by rearrangement of the intermediate product.



Although the formation of a solid from monovinylacetylene by the action of  $\alpha$ -particles has been reported by Heisig,<sup>67</sup> from the industrial viewpoint the most important property of monovinylacetylene is its conversion into monohalobutadiene by combination with hydrogen chloride or hydrogen bromide, a reaction

<sup>60</sup> W. S. Calcott and F. B. Downing, U. S. P. 1,876,857, Sept. 13, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 103. *British P.* 401,878, 1933; *Chem. Abs.*, 1934, 28, 2728. *French P.* 43,351, 1934, addn. to 733,663. *Chem. Abs.*, 1934, 28, 6727.

<sup>61</sup> J. A. Nieuwland, U. S. P. 1,926,055 and 1,926,056, Sept. 12, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5750. *British P.* 390,179, 1931; *Chem. Abs.*, 1933, 27, 4541. *French P.* 41,454, 1931; *Chem. Abs.*, 1933, 27, 2696. *German P.* 539,561, 1933; *Chem. Abs.*, 1934, 28, 2367.

<sup>62</sup> *British P.* 401,678, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 2728. <sup>63</sup> F. B. Downing, A. S. Carter and D. Hutton, U. S. P. 1,928,039, Sept. 12, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5755.

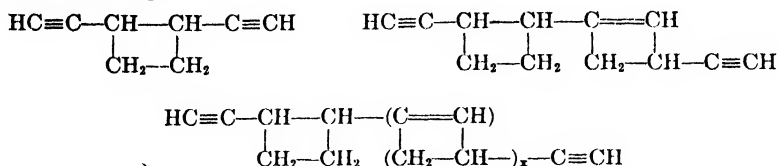
<sup>64</sup> G. A. Perkins and W. J. Toussaint, U. S. P. 1,971,650, Aug. 28, 1934, to Carbide & Carbon Chem. Corp.; *Chem. Abs.*, 1934, 28, 6446.

<sup>65</sup> A. S. Carter, U. S. P. 1,896,161, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 2458. *British P.* 388,402, 1931; *Brit. Chem. Abs. B.* 1933, 379. *French P.* 719,309, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 3265. R. F. Conaway, U. S. P. 1,967,225, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5834.

<sup>66</sup> R. A. Jacobson, H. B. Dykstra and W. H. Carothers, *J.A.C.S.*, 1934, 56, 1169.

<sup>67</sup> G. B. Heisig, *J.A.C.S.*, 1931, 53, 4460.

discussed later. Under pressure, vinylacetylene is readily polymerized by heat to form viscous drying oils<sup>58</sup> and finally hard, resinous polymers. All the nonresinous substances formed in this way contain acetylenic hydrogen and probably possess formulas of the types:<sup>59</sup>

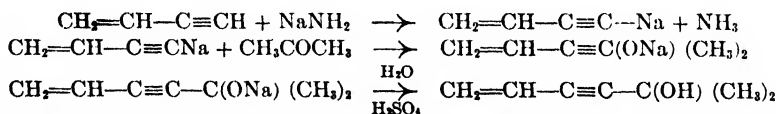


In the presence of acids, a considerable amount of styrene is formed also. This may be considered as a dimer of monovinylacetylene.

Polymerization may be controlled so as to yield an oily polymer which is completely nonvolatile at 100°C. under ordinary pressure. The danger of forming explosive compounds may be avoided by carrying out the reaction in a nonoxidizing atmosphere as was reported by Calcott and Downing.<sup>60</sup> The synthetic drying oil will absorb oxygen and halogens, the rate of reaction being greater, the lower the degree of polymerization. On the other hand the polymerization may be carried to the hard, brittle, resinous stage. Such a hard resin is obtained by heating vinylacetylene with 1 per cent of benzoyl peroxide for 200 hours at 110°C. It is insoluble in all solvents and does not react with the oxygen of the air or with halogens. Moreover, it is practically unchanged by treatment with strong sulphuric acid, strong alkalis or other corrosive agents, but is slowly oxidized by strong nitric acid.<sup>61</sup> The nonvolatile, liquid polymers constitute a class of drying oils suitable for compounding as paints and lacquers. The properties and use of these polymers are described later along with those of similar products from divinylacetylene.

### VINYLA CETYLENE DERIVATIVES

The preparation of vinylacetylides<sup>62</sup> from vinylacetylene and alkali metal amides (e.g., sodamide) has made possible the synthesis of a wide variety of vinyl ethynyl derivatives. Included among these are the carbinols (obtained by reaction between the acetylide and ketones or aldehydes) which polymerize readily to transparent resins.<sup>63</sup> The following reactions take place when sodamide and acetone are employed:



<sup>58</sup> A. S. Carter and F. B. Downing, U. S. P. 1,896,162, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 2591. See also O. Jordan, H. Hopff and E. Kühn (German P. 583,306, 1933; addn. to 580,234, to I. G. Farbenind. A.-G.); *Chem. Abs.*, 1934, 28, 1559) for the preparation of lacquers. W. S. Calcott, A. S. Carter and F. B. Downing (U. S. P. 1,950,430, March 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3272) for the impregnation of porous materials with vinylacetylene with subsequent polymerization of the latter.

<sup>59</sup> H. B. Dykstra, *J.A.C.S.*, 1934, 56, 1625. cf. M. E. Cupery and W. H. Carothers, *ibid.*, 1167.

<sup>60</sup> W. S. Calcott and F. B. Downing, U. S. P. 1,924,979, Aug. 29, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5341. British P. 334,655, 1932; *Chem. Abs.*, 1933, 27, 4252. French P. 733,681; *Chem. Abs.*, 1933, 27, 1011. German P. 601,504, 1934; *Chem. Abs.*, 1934, 28, 7624.

<sup>61</sup> A. S. Carter and F. B. Downing, U. S. P. 1,896,162, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 2591. British P. 385,933, 1931; *Brit. Chem. Abs. B*, 1933, 216.

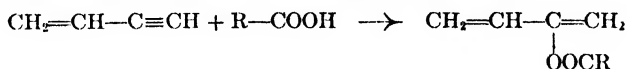
<sup>62</sup> W. H. Carothers and R. A. Jacobson, U. S. P. 1,963,934, June 19, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5081. W. H. Carothers and G. J. Berchet, U. S. P. 1,963,935, June 19, 1934; *Chem. Abs.*, 1934, 28, 5082.

<sup>63</sup> W. H. Carothers, G. J. Berchet and R. A. Jacobson, U. S. P. 1,963,074, June 19, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 4948.

One method for making the vinylacetylide is to add powdered sodamide to a solution of monovinylacetylene in liquid ammonia, benzene or an ether. The mixture is stirred several hours and the solvent then evaporated, leaving a white powder (sodium vinylacetylide). Substitution of lithium or potassium amide for sodamide gives analogous products. All of these alkali vinylacetylides are highly reactive toward air, water and carbon dioxide. Hence it was found advisable, in forming vinyl ethinyl compounds, to add the acetone (or other reagent) directly to the acetylide before the latter had been isolated from the solvent, or even to carry out the two reactions simultaneously. For example, 15 mols of acetone and 18.8 mols of vinyl acetylene were thoroughly mixed (keeping the reaction vessel cold) and 16.5 mols of powdered sodamide added over a period of two hours. Following 4 hours more stirring, a large quantity of water was added carefully. The oily layer which formed was separated, washed with dilute sulphuric acid and distilled. A yield of 898 g. of vinyl ethinyl dimethyl carbinol (b.p. 67°C. at 24 mm.) was secured. Methyl ethyl ketone, methyl octyl ketone, acetaldehyde and butyraldehyde formed homologous products. Crotonaldehyde, benzophenone and acrolein reacted to give resinous solids, due probably to polymerization during the condensation.

Vinylethinylcarbinols were found to polymerize readily in light and air, reaction being accelerated by metallic halides, oxidation accelerators (benzoyl peroxide, sodium perborate) and by catalysts of photochemical polymerization, e.g., uranyl nitrate. The ultimate product is a hard, insoluble, glass-like resin, but the intermediate stages range from thin syrupy substances to rubbery solids, all soluble in organic solvents but capable of further hardening. It is stated that polymerized carbinols, as well as the intermediate products, are compatible with nitrocellulose, drying oils and resins thus indicating their possible use in the preparation of lacquers, enamels, impregnants, varnishes and molded articles. For example, a light polymer was made by exposing a solution of equal parts of methyl ethyl vinyl ethinyl carbinol and toluene, containing 0.5 per cent benzoyl peroxide, to a Cooper-Hewitt light for 62 hours. The colorless solution (50 parts) was then mixed with lacquer thinner (100 parts) and pyroxylin base (57.8 parts). A dry film resulted after one hour at room temperature.

The ester derivatives of vinylacetylene present another source of resinous bodies. Organic carboxylic esters of 1,3-butadienol were prepared by Werntz<sup>64</sup> by passing monovinylacetylene into the organic acid. A mercury salt (mercuric sulphate) served as a catalyst, usually assisted by sulpho-acetic acid and acetic anhydride. The reaction proceeds according to the scheme:



For example, 10 g. of mercuric oxide were dissolved in 200 g. of hot glacial acetic acid and 10 g. of acetic anhydride added after cooling. Four grams of fuming sulphuric acid were then run in slowly, with stirring, to precipitate finely divided mercuric sulphate. Into this agitated mixture was fed a slow stream of monovinylacetylene, 1.5 hours being required for the addition of 173 g. The initial temperature was 12°C. but this was lowered to 0-5°C. by use of an ice bath and was so maintained during the reaction. All of the monovinylacetylene was absorbed. The resultant liquid was poured into a saturated salt solution, causing separation of a brown oil. On washing and vacuum distilling, 13 g. of liquid (b.p. 32-70°C. at 12 mm.) were secured.

Similar reactions were carried out using butyric, formic and chloroacetic acids.

<sup>64</sup> J. H. Werntz, U. S. P. 1,963,108, June 19, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 4745. See also J. H. Werntz, *J.A.C.S.*, 1935, 57, 204.

At 25°C. the yields were somewhat higher than at 0-5°C. but appreciable amounts of resin were also formed.

Esters of butadienol polymerize spontaneously, but the action is accelerated by pressure, heat, light and catalysts (acids, alkalies, peroxides, stannic chloride). The products, depending on the degree of polymerization, may be soluble resinous bodies, less soluble rubbery substances or insoluble materials resembling vulcanized rubber. Their properties vary somewhat depending on the organic acid used and may be further modified by the admixture of fillers, drying oils, natural or synthetic resins, plasticizers and cellulose nitrate or acetate. The resinous polymer form, made by heating the ester in an organic solvent, dries and further polymerizes to a clear, dry, flexible film, indicating the possibility of use in varnishes, lacquers and impregnants. Molding compositions containing the partially polymerized resins were also suggested. An emulsion of the original ester may be heated to create a latex reported to be comparable with natural rubber.

#### DIVINYLACETYLENE

This is a colorless liquid, which possesses an unusual allhaceous odor and rapidly assumes a straw color on exposure to light. It boils at 83.5°C. under 760 mm. and at 50° under 240 mm.,  $D_4^{20} = 0.7851$ .<sup>65</sup> Its chemical constitution can be inferred from the fact that it is reduced to n-hexane, does not contain an acetylenic hydrogen and yields on bromination two stereo-isomeric hexabromo-3-hexenes, melting at 81° and at 114°. The presence of two vinyl groupings is shown by its ready combination with two molecules of thio-p-cresol to furnish 1,6-di-(p-tolylthio)-3-hexyne, melting at 74.5-75.5°. On chlorination it is converted into a complex mixture of chlorides up to a hexachloride.<sup>67</sup> Treatment with aqueous hydrochloric acid gives first a monohydrochloride and then, very rapidly, a dihydrochloride, the latter substance having the constitution,<sup>68</sup>  $\text{CH}_3\text{—CH=CH—CCl=CH—CH}_2\text{Cl}$ . Although pure divinylacetylene undergoes thermal decomposition at 105-110°, yet it may be polymerized smoothly at lower temperatures in an inert atmosphere to viscous and, finally, hard, brittle, resinous polymers.

The most important application of divinylacetylene is in the production of synthetic drying oils which give coatings very resistant to corrosion by most chemical reagents. When divinylacetylene is exposed to air it rapidly absorbs oxygen to form highly explosive, peroxide-like compounds which have been found to detonate with violence on standing. Under the influence of heat, or by aging at ordinary temperatures, in the presence of air, divinylacetylene is transformed successively into an oily product, largely soluble in alcohol and acetone, to a gelatinous material, soluble in acetone and partly insoluble in alcohol, then to a resinous mass, insoluble in alcohol and slightly soluble in acetone, and finally to a hard, brittle polymer completely insoluble in acetone and alcohol. In preparing these products the formation of explosive substances is prevented by maintaining the temperature well below 113°C., best at 85-87°C.<sup>69</sup>

A synthetic drying oil has been made by Collins<sup>70</sup> through polymerization of

<sup>65</sup> J. A. Nieuwland, W. S. Calcott, F. B. Downing and A. S. Carter, *loc. cit.* See also R. Lespieau and Guillemonat, *Compt. rend.*, 1932, 195, 245; *Chem. Abs.*, 1932, 26, 5062, and R. Lespieau, Guillemonat and Urien, *Kolloid-Z.*, 1933 63, 84; *Chem. Abs.*, 1933, 27, 3193.

<sup>66</sup> W. H. Carothers, *J.A.C.S.*, 1933, 55, 2008.

<sup>67</sup> D. D. Coffman and W. H. Carothers, *J.A.C.S.*, 1933, 55, 2040.

<sup>68</sup> D. D. Coffman, J. A. Nieuwland and W. H. Carothers, *J.A.C.S.*, 1933, 55, 2048.

<sup>69</sup> J. A. Nieuwland, U. S. P. 1,812,541, June 30, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 5049.

<sup>70</sup> A. M. Collins, U. S. P. 1,812,544, June 30, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 5049.



divinylacetylene by heat. Thus a 12-18 per cent yield of viscous, non-volatile oil is produced by boiling divinylacetylene for 4 hours in the presence of air under a reflux apparatus (temperature of the boiling liquid, 85-90°C.) and distilling off unchanged divinylacetylene under reduced pressure. Alternatively, a mixture of 75 per cent of divinylacetylene and 25 per cent of a tetramer of acetylene is boiled with refluxing at 75-80° at atmospheric pressure for 5 hours in an atmosphere of nitrogen. An equal weight of xylene is added and the mixture distilled, leaving as a residue a clear reddish-orange liquid of relatively low viscosity, having good drying properties and requiring no thinning before use. The yield in this case is about 50 per cent based on the acetylene mixture used. Some acetylene tetramer in the raw material is said to be advantageous in increasing the yield of drying oil. A lacquer which can be brushed on metals is obtained by mixing 500 g. of a 50 per cent solution of polymers (obtained from divinylacetylene and tetramer) in xylene with 100 g. of a 50 per cent solution of metastyrene in the same solvent.

Polymerization of both vinylacetylene and divinylacetylene while in the form of a flowing stream has been described by Calcott and Downing.<sup>71</sup> In the production of drying oils from divinylacetylene and acetylene tetramer by polymerization, better results are secured by effecting reaction in the presence of an added solvent at the boiling point.<sup>72</sup> A 25 per cent yield of drying oil is obtained by refluxing a mixture of equal weights of pure divinylacetylene and xylene for 24 hours at 85-90°C. in the presence of air. By heating the tetramer of acetylene in a closed vessel at 100° for 3 hours, an almost quantitative yield of a practically non-volatile oil is secured. This oil is used as a lacquer or varnish. A practically complete conversion into film-forming polymers is also obtained by boiling 40 g. of dibutylamine, 1000 g. of crude divinylacetylene, containing 40 per cent of tetramer, and 1000 g. of xylene under reflux in an atmosphere of nitrogen for 50 hours. The product in this case is a clear, reddish orange liquid of relatively low viscosity, having good drying properties and requiring no thinning before use. Collins found that non-volatile liquid materials in any stage of polymerization between that represented by an average molecular weight of 156 and that just short of the formation of a gel can be used as synthetic drying oils.

The synthetic drying oils produced by partial polymerization of divinylacetylene and the tetramer of acetylene have been marketed under the name "S-D-O."<sup>73</sup> This coating composition consisted of a solution of the partially polymerized acetylene polymer in an aromatic hydrocarbon solvent. The pure polymers themselves continued to polymerize at normal temperatures, even in the absence of air. However, when diluted with a solvent, spontaneous polymerization did not occur and the material could be stored at normal temperatures in the absence of air and light. When applied to a surface, the solvent rapidly evaporated leaving a film of "S-D-O" base which dried out quickly to a hard, transparent, amber-colored resin. Drying out was much more rapid than with the usual drying oils because polymerization was accelerated by a very small amount of absorbed oxygen. The dried films were more impervious to moisture than equally thick films of linseed oil paint<sup>74</sup> and were not attacked by chlorine, bromine, brine, ammonia (either anhydrous or in solution), hydrogen sulphide, crude oil or refined petroleum. The only chemicals that did attack these polymerized films were strong oxidizing

<sup>71</sup> W. S. Calcott and F. B. Downing, U. S. P. 1,950,429, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3271.

<sup>72</sup> A. M. Collins, U. S. P. 1,812,849, June 30, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 5048.

<sup>73</sup> O. M. Hayden, *Ind. Eng. Chem.*, 1932, 24, 563; see also *Chem. Met. Eng.*, 1932, 39, 517.

<sup>74</sup> H. Scheiber (*Farbe u. Lack*, 1934, 326, 339; *Brit. Chem. Abs.* B, 1934, 803) finds, however, that drying oils prepared from polyvinyl compounds are inferior to natural oils from the standpoint of adhesion, as well as in the toughness and hardness of the dry film.

agents, such as concentrated hydrogen peroxide, chromic acid, nitric acid and hot, concentrated, sulphuric acid. Hydrofluoric acid penetrated these films but did not destroy them. The fully polymerized films were not thermoplastic and withstood temperatures as high as 200°C. without change. These synthetic drying oils can be applied as paints to almost any surface other than glass or enamel. Laboratory tests indicated the possibility of using this type of protective covering for silo walls.<sup>76</sup> In using "S-D-O" paints, successive coatings must be applied before the previous coat has fully hardened or else preceding coats must be treated similar to a metal surface, i.e., roughened by a sand-blast or other means.

Toxic coatings for ship bottoms were suggested by Calcott and Downing<sup>76</sup> as an application for synthetic drying oils from acetylene polymers. Toxicity is supplied by incorporation of isopropyl-naphthalene or dinitrochlorobenzene in the composition. Divinylacetylene may be converted into a rubber-like material by a process due to Calcott, Downing and Powers.<sup>77</sup> The divinylacetylene is first emulsified with water to give an emulsion of grain size similar to that of natural Hevea rubber latex, or approximately a diameter of 1 micron. This emulsion is then polymerized either by allowing it to stand at 30°C. for a week, by heating or by the addition of sufficient 2 per cent acetic acid to change the  $pH$  to about 4. The coagulum is freed from water by milling and is ready for use as a rubber substitute. Physically the products obtained from divinylacetylene in this manner are said to resemble raw rubber and are characterized by a high degree of elasticity.

According to Calcott, Carter and Downing,<sup>78</sup> divinylacetylene may be partially hydrogenated (using a nickel catalyst) and the resulting material polymerized (with benzoyl peroxide) to secure resins soluble in organic solvents and stable to light. Compounds of this type, either alone or mixed with natural gums and resins, can be incorporated with pigments, drying oils, volatile solvents and fillers to form paints and varnishes.

#### HALOGENATED DERIVATIVES OF ACETYLENE POLYMERS AND THEIR APPLICATION

Considerable technical and scientific interest is centered round the products obtained by treating monovinylacetylene with halogen acids since it has been found that the resulting halogenobutadienes are capable by controlled polymerization of being converted into rubber-like materials of great industrial promise. On shaking monovinylacetylene with aqueous concentrated hydrochloric acid, two compounds are produced, namely 4-chloro-1,2-butadiene and 2-chloro-1,3-butadiene, or "chloroprene," as the latter substance has been named. The former compound is probably the initial product of the reaction, but it speedily undergoes isomerization to chloroprene especially in the presence of certain catalysts. The most active catalyst mentioned is a solution of cuprous chloride in hydrochloric acid.<sup>79</sup> Accordingly, the reaction between vinylacetylene and hydrochloric acid in the presence of cuprous chloride at 0-20°C. gives almost quantitative yields of chloroprene in a few hours. On prolonged contact of vinylacetylene with hydrochloric acid especially with cuprous chloride as a catalyst, two molecules of hydrochloric acid are

<sup>76</sup> G. F. Steigerwalt, *Agr. Eng.*, 1933, 14, 154; *Chem. Abs.*, 1934, 28, 873.

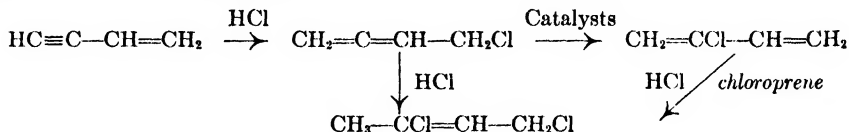
<sup>77</sup> W. S. Calcott and F. B. Downing, U. S. P. 1,958,418, May 15, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 4615.

<sup>78</sup> W. S. Calcott, F. B. Downing and D. H. Powers, U. S. P. 1,329,502, Oct. 27, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 876. *British P.* 389,109, 1933; *Chem. Abs.*, 1933, 27, 4717.

<sup>79</sup> W. S. Calcott, A. S. Carter and F. B. Downing, U. S. P. 1,959,353 and 1,959,408, May 22, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 4434, 4615.

<sup>80</sup> W. H. Carothers, G. J. Berchet and A. M. Collins, *J.A.C.S.*, 1932, 54, 4066. See also W. H. Carothers and G. J. Berchet, *J.A.C.S.*, 1933, 57, 2807.

added with the formation of 2,4-dichloro-2-butene. The complete reaction scheme may be formulated as follows:



The original method of Carothers and Collins<sup>80</sup> which involved shaking the catalyst and reactants in batches was later transformed by Downing, Carter and Hutton<sup>81</sup> into a continuous process. The latter is similar to that for the preparation of vinylacetylene<sup>82</sup> in that the reactants are passed continuously over the catalyst solution heated between 30-60°C. The products are removed by the stream of unreacted vinylacetylene and condensed. The vinylacetylene is then returned to the reaction vessel. Either chloroprene or 2,4-dichloro-2-butene may be formed. Rapid passage of the gases favors the formation of chloroprene, over 90 per cent yield being obtained. Collins<sup>80</sup> has combined the transformation of acetylene to vinylacetylene and the latter to chloroprene into one step. The distillate from the reaction mixture contains 24.3 per cent of chloroprene, 30.2 per cent of divinylacetylene and 30.0 per cent monovinylacetylene which are separated by fractional distillation. The laboratory preparation of chloroprene has been described by Carothers, Berchet and Collins<sup>84</sup> and by Zelinski, Kozlov and Shter.<sup>85</sup>

Of the two monohydrochlorides of vinylacetylene, only chloroprene is of industrial importance. The accompanying isomer, 4-chloro-1,2-butadiene is a colorless liquid boiling at 87.7-88.1°C. and shows no tendency to polymerize.<sup>86</sup> It can be stored unchanged for many months under laboratory conditions and even undergoes no change when submitted to a pressure of 6000 atmospheres for 45 hours at 50°.<sup>87</sup> On the other hand, chloroprene possesses an unusually pronounced tendency to polymerize to rubber-like substances, some of which would appear to have industrial possibilities.

Chloroprene,  $\text{CH}_2=\text{CCl}-\text{CH}=\text{CH}_2$ , is a colorless liquid of  $d_4^{20}$  0.9583 and boiling at 59.4°C. under 760 mm. The presence of a conjugated system of double bonds in the molecule of this compound is demonstrated by its ready combination with maleic anhydride and naphthoquinone to furnish crystalline addition products.<sup>88</sup>

As previously mentioned, chloroprene is distinguished by its rapid change to rubber-like and resinous products,<sup>89</sup> transformation being complete in a few days. In comparison, the spontaneous polymerization of isoprene requires several years for completion. In the case of chloroprene, conversion is greatly accelerated by

<sup>80</sup> W. H. Carothers and A. M. Collins, U. S. P. 1,950,431, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3271. French P. 721,532, 1931; *Chem. Abs.*, 1932, 26, 4061. British P. 387,325, 1931; *Brit. Chem. Abs. B*, 1933, 296.

<sup>81</sup> F. B. Downing, A. S. Carter and D. Hutton, U. S. P. 1,950,434, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3271. British P. 395,131, 1933; *Chem. Abs.*, 1934, 28, 375. French P. 41,933, 1933; *Chem. Abs.*, 1933, 27, 4538. German P. 583,708, 1933; *Chem. Abs.*, 1934, 28, 2015.

<sup>82</sup> W. S. Calcott and F. B. Downing, U. S. P. 1,876,857, Sept. 13, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 103.

<sup>83</sup> A. M. Collins, U. S. P. 1,950,435, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3270.

<sup>84</sup> W. H. Carothers, G. J. Berchet and A. M. Collins, *loc. cit.*

<sup>85</sup> N. D. Zelinsky, N. S. Kozlov and R. S. Shter, *Bull. Acad. Sci. U. S. S. R.*, 1934, 8, (1), 141; *Chem. Abs.*, 1934, 28, 5713. See also N. D. Zelinsky, N. S. Kozlov, R. S. Shter and N. G. Pesin, *Sintet. Kauchuk*, 1932, (3), 4; *Chem. Abs.*, 1933, 27, 606.

<sup>86</sup> 1-Chloro-1,3-butadiene, however, is reported to polymerize forming rubber-like masses. British P. 421,146, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1935, 195.

<sup>87</sup> This is curious since M. Bourguet (*Compt. rend.*, 1931, 192, 686; *Chem. Abs.*, 1931, 25, 2980) found that phenylpropadiene polymerized rapidly at 60°C. to a soft resin.

<sup>88</sup> W. H. Carothers, I. Williams, A. M. Collins and J. E. Kirby, *J. A. C. S.*, 1931, 53, 4203.

<sup>89</sup> W. H. Carothers and A. M. Collins, U. S. P. 1,950,432, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3271. I. Williams U. S. P. 1,950,436, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3271. British P. 387,363; *Chem. Abs.*, 1933, 27, 4718.



keeping the concentration of the polymer below 15-18 per cent through the addition of solvent from time to time. Carothers, Collins and Kirby<sup>90</sup> polymerized 2-chloro-1,3-butadiene in a number of different solvents. These included volatile liquids (benzene, toluene, ether, ethylene chloride and carbon disulphide), non-volatile oils (mineral oil, cottonseed oil, ethyl benzoate, corn oil and cod-liver oil) which remain in the polymer and modify its properties, and solvents which precipitate the resin as it is formed (ethyl alcohol). In this manner not only can polymerization be controlled, but a wide variation is also possible in the nature and application of the resulting substances. In addition, co-polymers of the chlorobutadiene with styrene, isoprene or tung oil have been formed. The latter products were said to be plastic and usually transparent.

Several other types of amorphous polymers of chloroprene have been recognized by Carothers and his co-workers but the most important from an industrial standpoint are the  $\alpha$ - and  $\mu$ -polymers.

$\alpha$ -Polychloroprene is best obtained by exposing chloroprene to strong illumination from a Mazda lamp or a mercury arc at 35°C. for twenty-four hours. Under these conditions about 30 per cent of the chloroprene is polymerized and the  $\alpha$ -polymer can be isolated by pouring into alcohol. This polymer is plastic and dissolves completely in benzene to form highly viscous solutions. It can be calendered into thin sheets or extruded with the usual rubber material. At 30°C. the  $\alpha$ -polymer is completely changed in 48 hours (or in 5 minutes at 130°C.) into the  $\mu$ -polymer. This change, which corresponds to the vulcanization of rubber, does not require the addition of sulphur but can be effected by heat alone and is accelerated by zinc chloride or butyrate, ferric chloride, or primary aromatic amines. Transformation of chloroprene occurs very readily also in aqueous emulsion and the product constitutes a synthetic (vulcanized) latex<sup>91</sup> which has about the same particle size as good Hevea latex and may be used in much the same way.

One method for preparing the latex is to agitate 2-chloro-1,3-butadiene with an equal weight of water in which has been dissolved 2 per cent by weight of sodium oleate.<sup>92</sup> Heat is evolved as the emulsion forms and the mixture must be cooled. A milk-white suspension results in which the particles show a definite Brownian movement. Polymerization is complete after a few hours, but may be retarded by small amounts of iodine or catechol. In this case the dispersed bodies are plastic, soluble in benzene and resemble natural unvulcanized rubber. As in the natural latex, precipitation or coagulation may be accomplished by addition of acid. Ordinary rubber antioxidants (aromatic amines and phenols) as well as acid acceptors (alkalies, zinc oxide, sodium oleate) are said to inhibit oxidation of the synthetic material. The use of protective colloids, i.e., casein, albumen, natural latex serum, pectins and gum arabic, in the latex is also recommended.

Barrett and Dorough<sup>93</sup> replaced sodium oleate with the sodium or ammonium salt of glyceryl phthalate resin. In some instances the polybasic acid was blended with 20-35 per cent of castor oil, stearin, tung oil or cottonseed oil previous to esterification. Chloroprene latices prepared in this manner are said to give films with improved tensile strength, tear resistance and elasticity.

By incorporating 2 per cent of an oxidizing agent, e.g., potassium persulphate

<sup>90</sup> W. H. Carothers, A. M. Collins and J. E. Kirby, U. S. P. 1,967,860, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 6026.

<sup>91</sup> W. S. Calcott, F. B. Downing and D. H. Powers, U. S. P. 1,903,500, Apr. 11, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 3358. See also British P. 387,340 and 393,172, 1933; *Chem. Abs.*, 1933, 27, 4717; 1934, 28, 372.

<sup>92</sup> A. M. Collins, U. S. P. 1,967,861, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 6026.

<sup>93</sup> H. J. Barrett and G. L. Dorough, U. S. P. 1,967,220, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 6025.

or sodium perborate, with a sodium oleate dispersion of chloroprene, Collins<sup>100</sup> is reported to have secured coagulated films and threads which on drying showed improved tensile strength, especially after aging at 80°C.

$\alpha$ -Polychloroprene has been placed on the market in the form of a synthetic rubber named DuPrene.<sup>101</sup> This product has excited a vast amount of interest,<sup>102</sup> and numerous studies have been made comparing it to natural rubber<sup>103</sup> and investigating the compounding of DuPrene with other substances to improve its



g. 46.

Flex-Cracking Test of DuPrene. Natural rubber shown in background for comparison. Rubber cracks considerably in this flex test but DuPrene does not. (E. R. Bridgwater.)

*Courtesy Industrial and Engineering Chemistry*

resistance to various conditions.<sup>104</sup> The following properties of DuPrene and its comparison with rubber are of note:

1. Compounds using DuPrene are not swelled nearly as much as corresponding rubber compounds are in petroleum distillates. While unsaturated compounds like oleic acid have almost the same swelling effect on DuPrene products as on rubber ones, the swollen DuPrene retains most of its toughness and tear-resistance. Carbon tetrachloride and aromatic hydrocarbons swell and cause some tendering of DuPrene, but the effect is not as great as on rubber.<sup>105</sup>
2. Overcuring DuPrene compounds does not ruin the aging properties as it does with rubber compounds.
3. Sulphur is not essential for the vulcanization of DuPrene.
4. Cements made by swelling DuPrene in appropriate solvents are better adhesives than those made from rubber.
5. Rubber compounds decline sharply in abrasion resistance with increasing temperature whereas DuPrene ones do not.
6. DuPrene is less permeable to gases than rubber.
7. It is more resistant to ozone.
8. It is not deteriorated by flexing in the way that rubber is. In one test the rubber sample broke through after 24 hours whereas the DuPrene after 80 hours showed no indication of failure. (See Fig. 46.)

<sup>100</sup> A. M. Collins, U. S. P. 1,967,865, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 6027.

<sup>101</sup> *Ind. Eng. Chem. News Ed.*, 1931, 9, 321. DuPrene is made by E. I. du Pont de Nemours & Co. at Deepwater Point, N. J. DuPrene is also spelled Duprene.

<sup>102</sup> Reviews on the subject may be found in: R. Pummerer, *Angew. Chem.*, 1934, 47, 209; *Chem. Abs.*, 1934, 28, 4287. C. M. A. Stine, *J. S. C. I.*, 1933, 52, 416. C. A. Tyler, *Chem. Ind. (N. Y.)*, 1934, 34, (4), 303; *Chem. Abs.*, 1934, 28, 3038. A. Kubelnek, *J. Rubber Ind. (U. S. S. R.)*, 1933, 10, 72; *Chem. Abs.*, 1933, 27, 6016. W. Szukiewicz, *Przemysł Chem.*, 1934, 18, 22; *Chem. Abs.*, 1934, 28, 4628. *Oil, Paint and Drug Rep.*, 1931, Nov. 9, 17.

<sup>103</sup> W. J. S. Naunton, M. Jones and W. F. Smith, *Trans. Inst. Rubber Ind.*, 1933, 9, 169. *Chem. Abs.*, 1934, 28, 2569. E. R. Bridgwater, *Ind. Eng. Chem.*, 1934, 26, 33; O. M. Hayden and E. H. Krismann, *Ind. Eng. Chem.*, 1933, 25, 1219.

<sup>104</sup> E. R. Bridgwater and E. H. Krismann, *Ind. Eng. Chem.*, 1933, 25, 280. O. M. Hayden and E. H. Krismann, *loc. cit.*

<sup>105</sup> F. Kirchhof (*Chem.-Ztg.*, 1934, 58, 542; *Brit. Chem. Abs. B*, 1934, 774) found that aromatic solvents caused greater swelling of  $\mu$ -chloroprene (as well as of chlorinated and vulcanized rubber) than aliphatic solvents.

9. Properly compounded DuPrene is affected hardly at all by 50 per cent sulphuric acid. Boiling for 4 days in 50 per cent sulphuric acid reduced the tensile strength from 191.6 kg./sq. cm. only to 80.8 kg./sq. cm.
10. Caustic soda and other common alkalis have practically no effect.
11. In nerve and snap it resembles natural rubber more than any other synthetic product and like natural rubber it gives an x-ray diffraction diagram.<sup>106</sup>
12. On the other hand, Whitby and Katz<sup>107</sup> found that the samples examined by them suffered a more serious fall in strength with rise of temperature than did samples of natural rubber.<sup>108</sup>

In compounding DuPrene, De Holczer<sup>109</sup> recommended the use of the plastic substance produced by Shinkle<sup>110</sup> through the action of ethylene dichloride on aromatic hydrocarbons of the type  $R-C_6H_4-R'$ , where R and R' represent hydrogen or alkyl radicals of more than one carbon. This mixture is less likely to scorch on milling and is resistant to hot lubricating oil at 150°C.

A mixture of chlorinated drying oils and polymerized chlorobutadiene has been suggested for use in a rubber composition to render it fireproof.<sup>111</sup> Hepp<sup>112</sup> advises using polymerized chloroprene as a binding agent.

Porous materials, i.e., leather, wood, cloth and tile, are said to be made resistant to water by impregnation with chlorobutadiene, followed by polymerization *in situ*.<sup>113</sup> The chlorodiene may be diluted with benzene, alcohol, acetone or carbon tetrachloride. The partially polymerized form has also been employed, either in solution, as an emulsion or in a spreading composition for surface coating. Drying oils, softeners and other resins, when incorporated, serve to enhance the desired properties. Oilproof paper, window shades, awning cloth and book-binding materials are included in the suggested uses.<sup>114</sup>

The homologues<sup>115</sup> of chloroprene do not polymerize so readily as chloroprene and the products are soft, plastic and sticky.<sup>116</sup>

The addition of aqueous hydrogen bromide to vinylacetylene in the presence of cuprous bromide leads to the formation of 2-bromo-1,3-butadiene or "bromoprene."<sup>117</sup> This compound may also be made directly from acetylene<sup>118</sup> by bringing the latter into contact with an aqueous solution of cuprous bromide and hydrobromic acid. Polymerization of bromoprene is somewhat more rapid than that of chloroprene, but the products are strictly analogous. Spontaneous polymerization yields first a plastic polymer ( $\alpha$ -polybromoprene) and then finally  $\mu$ -polybromoprene, which resembles vulcanized rubber but is more dense than the rubber

<sup>106</sup> P. Garbsch and G. v. Susich, *Kautschuk*, 1932, 8, 122; *Chem. Abs.*, 1932, 26, 5906.

<sup>107</sup> G. S. Whitby and M. Katz, *Ind. Eng. Chem.*, 1933, 25, 1338.

<sup>108</sup> At 20°C. the strength was only slightly less than that of vulcanized natural rubber. At 37°C. the strength was seriously impaired and at 70° it was practically destroyed.

<sup>109</sup> L. J. De Holczer, U. S. P. 1,967,292, July 24, 1934, to New York Belting & Packing Company; *Chem. Abs.*, 1934, 28, 5941. British P. 421,435, 1934; *Brit. Chem. Abs.* B, 1935, 195.

<sup>110</sup> S. D. Shinkle, French P. 743,753, 1933, to Naugatuck Chemical Co.; *Chem. Abs.*, 1933, 27, 3789. British P. 407,948, 1934; *Chem. Abs.*, 1934, 28, 5190.

<sup>111</sup> D. F. Twiss, A. S. Carpenter and A. E. T. Neale, British P. 420,116, 1933, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs.*, B, 1935, 114.

<sup>112</sup> S. F. Hepp, U. S. P. 1,932,104, Oct. 10, 1933; *Chem. Abs.*, 1934, 28, 602.

<sup>113</sup> I. Williams, U. S. P. 1,967,275, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5943.

<sup>114</sup> A. M. Collins and L. L. Larson, U. S. P. 1,967,863, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5993. British P. 413,666, 1934; *Chem. Abs.*, 1935, 29, 255.

<sup>115</sup> R. A. Jacobson, U. S. P. 1,950,440, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3270. W. H. Carothers and D. D. Coffman, U. S. P. 1,950,441, Mar. 13, 1934; *Chem. Abs.*, 1934, 28, 3270. See also A. E. Favorski, Russian P. 31,015 to 31,017, 1933; *Chem. Abs.*, 1934, 28, 3425.

<sup>116</sup> W. H. Carothers and D. D. Coffman, *J.A.C.S.*, 1932, 54, 4071. R. A. Jacobson and W. H. Carothers, *J.A.C.S.*, 1933, 55, 1624.

<sup>117</sup> W. H. Carothers, A. M. Collins and J. E. Kirby, *J.A.C.S.*, 1933, 55, 786. W. H. Carothers and A. M. Collins, U. S. P. 1,950,431, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3271.

<sup>118</sup> A. M. Collins, U. S. P. 1,950,435, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3270.

of  $\mu$ -polychloroprene. At elevated temperatures in the presence of antioxidants, a volatile, liquid  $\beta$ -polymer is formed.<sup>119</sup>

Chloroprene, bromoprene and other  $\beta$ -substituted dienes, i.e., 2-phenyl-1,3-butadiene, were treated by Carothers and Collins<sup>120</sup> with maleic acid and anhydride, fumaric acid and other compounds containing a reactive C-C double bond. The resulting products were stated to be serviceable as intermediates for the synthesis of dyes, perfumes and medicinal compounds.

#### OTHER HALOGEN DERIVATIVES OF ACETYLENE POLYMERS

Derivatives obtained by reacting divinylacetylene with sulphur monochloride have been reported to be synthetic drying oils, suitable for protecting articles from corrosion.<sup>121</sup> Vinylacetylene polymers may be made less liable to change due to the oxygen of the air by reducing their unsaturation. This may be accomplished by catalytic reduction<sup>122</sup> or halogenation.<sup>123</sup> Reaction is not carried so far that the products may not still be polymerized into rubber-like masses.<sup>124</sup> Condensation of the acetylene polymers with sulphuryl chloride<sup>125</sup> (SO<sub>2</sub>Cl<sub>2</sub>) has also been said to yield materials, some of which can be used as drying oils and in coating compositions.

By-products from the preparation of chloroprene, e.g., 4-chloro-1,2-butadiene, may be further chlorinated, and then treated with alkali to form unsaturated chlorinated hydrocarbons which are readily polymerized.<sup>126</sup> Thus, 4-chloro-1,2-butadiene (in carbon tetrachloride at -50°C.) is converted into 1,2,3,4-pentachlorobutane. Treatment of the latter compound with alcoholic potassium hydroxide gives 1,2,3-trichloro-1,3-butadiene which in turn, at 90°, is transformed into a soft non-plastic, non-rubber-like mass. Co-polymerization of 1,2,3-trichloro-1,3-butadiene and 2-chloro-1,3-butadiene, however, yields a softer, rubber-like body. Homologues of vinylacetylene may be produced<sup>127</sup> and polymerized. The polymers are used in the same manner as those of vinylacetylene itself. Mercury<sup>128</sup> and halogen substituted<sup>129</sup> vinylacetylenes are known also and these change into dark tars and solids on long standing. Several of the polymers are explosive. Blomquist and Marvel<sup>130</sup> obtained viscous tars and amorphous substances from the re-

<sup>119</sup> W. H. Carothers, J. F. Kirby and A. M. Collins, *J.A.C.S.*, 1933, 55, 789. W. H. Carothers and A. M. Collins, U. S. P. 1,950,433, Mar. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3271.

<sup>120</sup> W. H. Carothers and A. Collins, U. S. P. 1,967,862, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5994.

<sup>121</sup> W. S. Calcott, A. S. Carter and F. B. Downing, U. S. P. 1,896,158, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 2591. Also W. S. Calcott and A. S. Carter, U. S. P. 1,896,157, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 259.

<sup>122</sup> W. S. Calcott, F. B. Downing and D. H. Powers, U. S. P. 1,903,500 and 1,903,501, Apr. 11, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 3358, 3222. British P. 389,108, 1933; *Chem. Abs.*, 1933, 27, 4700. W. S. Calcott, A. S. Carter and F. B. Downing, U. S. P. 1,920,242, Aug. 1, 1933; 1,959,408, May 22, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 4818; 1934, 28, 4615.

<sup>123</sup> W. S. Calcott and A. S. Carter, U. S. P. 1,896,159, Feb. 7, 1933 to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 2591. British P. 389,122, 1933; *Chem. Abs.*, 1933, 27, 4700. See also G. J. Berchet and W. H. Carothers, *J.A.C.S.*, 1933, 55, 2004.

<sup>124</sup> See D. D. Coffman and W. H. Carothers, *J.A.C.S.*, 1933, 55, 2040.

<sup>125</sup> W. S. Calcott and A. S. Carter, U. S. P. 1,896,160, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.*, B, 1933, 964.

<sup>126</sup> W. H. Carothers and G. J. Berchet, U. S. P. 1,965,369, July 3, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5716.

<sup>127</sup> W. H. Carothers and R. A. Jacobson, U. S. P. 1,963,934, June 19, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1051; *J.A.C.S.*, 1933, 55, 1097, 1622. W. H. Carothers and G. J. Berchet, U. S. P. 1,963,935, June 19, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5082; *J.A.C.S.*, 1933, 55, 1094; see also by the same authors *J.A.C.S.*, 1933, 55, 2813.

<sup>128</sup> W. H. Carothers, R. A. Jacobson and G. J. Berchet, *J.A.C.S.*, 1933, 55, 4665.

<sup>129</sup> R. A. Jacobson and W. H. Carothers, *J.A.C.S.*, 1933, 55, 4667. T. H. Vaughn and J. A. Nieuwland, *J.C.S.*, 1933, 741. W. H. Carothers and G. J. Berchet, *J.A.C.S.*, 1933, 55, 2807. See also R. A. Jacobson, U. S. P. 1,967,864, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5834.

<sup>130</sup> A. T. Blomquist and C. S. Marvel, *J.A.C.S.*, 1933, 55, 1655.



action of the homologues of divinylacetylene with bromine and maleic anhydride, respectively.

Iodine reacts readily with acetylene, vinylacetylene and their homologues in liquid ammonia.<sup>121</sup> Methylvinyliodoacetylene made in this manner was a colorless liquid, but on standing in the presence of oxygen it became dark and viscous, eventually forming a black solid.

#### RESINOUS CONDENSATION AND POLYMERIZATION PRODUCTS OF ACETYLENE

Synthetic resins have been produced by Deutsch, Haehnel and Herrmann<sup>122</sup> by condensing acetylene with organic substances in the presence of salts of mercury or aluminum. If necessary, these catalysts were activated with acids or alkalis. The organic substances include aliphatic and aromatic hydrocarbons,<sup>123</sup> phenols, carboxylic acids and their esters. The products are either water-insoluble resins or substances of the cuprene type. For example, acetylene is introduced into an emulsion of mercury benzene sulphinate in glacial acetic acid, the mixture heated after absorption and then leached to yield a resin. By passing acetylene into an emulsion of amyl alcohol and mercury sulphate until absorption ceases, a liquid mass is obtained which, after decantation, can be used directly as a lacquer, or the resin can be isolated therefrom by distilling off the amyl alcohol. A cuprene-like substance is formed by introducing acetylene into an emulsion of aluminum chloride in dry benzene, mixing the product with water and steam-distilling off the benzene. Acetylene is passed into a heated mixture of hexane and mercury sulphate and the mixture heated for several hours. Removal of hexane by distillation yields a solid resin.

Bourgoin<sup>124</sup> made plastic substances applicable for electrical insulation by treating animal and vegetable fats mixed with calcium carbide with steam under pressure. Acetylene first forms which then reacts with the fatty substance. With cuprous chloride as a catalyst, Durand and Banos succeeded in condensing acetylene and carbon monoxide in pyridine solution to a black tar.<sup>125</sup> Quinone was identified as one of its constituents. Another resin from acetylene was obtained by Quilico and Freri by the action of fuming nitric acid on acetylene. They<sup>126</sup> obtained among other products an explosive substance,  $C_4H_2N_6O_7$ . This when dissolved in ethyl alcohol gives, with aniline, after evaporation of the solvent, a pitch-like mass.

#### RESINOUS SUBSTANCES FROM OTHER ACETYLENE HYDROCARBONS

Many of the higher homologues of acetylene are converted into resinous substances by polymerization either spontaneously or under the influence of heat, light, catalysts and silent electric discharges. Methylacetylene (propyne) changes to a white solid when exposed to a hot mercury-arc light.<sup>127</sup> By exposing 1-heptyne to the action of the silent discharge, Losanich<sup>127</sup> obtained along with liquid polymers

<sup>121</sup> T. H. Vaughn and J. Nieuwland, *J.A.C.S.*, 1932, 54, 787; 1934, 56, 1207.

<sup>122</sup> H. Deutsch, W. Haehnel and W. O. Herrmann, German P. 493,324, 1924, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1930, 24, 2758. British P. 228,157, 1924; *Chem. Abs.*, 1925, 19, 2752. Canadian P. 256,557, 1925; *Chem. Abs.*, 1926, 20, 2333.

<sup>123</sup> In the endeavor to obtain isoprene by heating acetylene and propylene under pressure, polymerization occurred in part to bodies capable of use as varnish or turpentine substitutes. H. O. Traun, British P. 156,116, 1920; *J.S.C.I.*, 1922, 41, 436A.

<sup>124</sup> L. G. Bourgoin, U. S. P. 1,567,785, Dec. 22, 1925; *Chem. Abs.*, 1926, 20, 607. British P. 265,677, 1925; *Brit. Chem. Abs.*, B, 1927, 253.

<sup>125</sup> J. F. Durand and M. Banos, *Compt. rend.*, 1927, 184, 972; *Chem. Abs.*, 1927, 21, 2467.

<sup>126</sup> A. Quilico and M. Freri, *Gazz. chim. ital.*, 1929, 59, 930; 1930, 60, 721; *Chem. Abs.*, 1930, 24, 3484; 1931, 25, 1247. For other nitrogen-containing resins see Chapter 35.

<sup>127</sup> S. C. Lind and R. Livingston, *J.A.C.S.*, 1933, 55, 1036.

<sup>128</sup> S. M. Losanich, *Bull. soc. stiin. Bucharest*, 1914, 23, 3; *Chem. Abs.*, 1917, 11, 254.

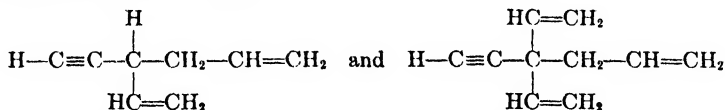
a dark-red, thick mass soluble in ether and benzene. Under similar conditions, 1-octyne gave a dark-red, soft mass, soluble in ether and benzene but insoluble in alcohol and having a molecular weight corresponding to a "nonaoctyne,"  $(C_8H_{11})_n$ .

When phenylacetylene is heated in a sealed tube for 23 hours at 230-240°C., it is converted into a tough, brown mass, soluble in ether. Alcohol precipitates an amorphous brown powder which, however, is readily soluble in most organic solvents.<sup>138</sup> When heated in a sealed tube with an aqueous solution of methylamine or ethylamine, phenylacetylene is converted into sym-triphenylbenzene. Under similar conditions, dimethylamine, trimethylamine, diethylamine and piperidine convert it into an oily substance. Aqueous ammonia and potassium hydroxide solutions likewise give tarry products.<sup>139</sup> Hunt and Turner<sup>140</sup> treated phenylacetylene with arsenious chloride and aluminum chloride. The resulting yellow liquid became black and viscous in 2 hours, but purification of the product yielded an amorphous yellow solid.

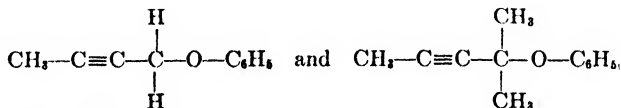
Diacetylene,  $CH\equiv C-C\equiv CH$ , is a very interesting hydrocarbon which is produced in small amounts during the electropyrrolysis of acetylene, methane, petroleum hydrocarbons and alcohol, and also in the thermal decomposition of acetylene, methane and other materials at very high temperatures. This hydrocarbon readily polymerizes above 0°C. with the formation of an insoluble brown mass which does not melt at 350°C. but explodes at higher temperatures.<sup>141</sup> When preserved in sealed tubes at 0°, in the absence of light, the hydrocarbon is transformed into a dark brown polymer, which explodes violently on contact with a hot wire.<sup>142</sup> Liquid products are formed from diacetylene at higher temperatures.<sup>143</sup> The analogous compound, dipropargyl<sup>144</sup> (1,5-hexadiyne) rapidly polymerizes to a solid hydrocarbon.

A number of hydrocarbons which contain both ethylenic and acetylenic bonds in other than the 1,3-position polymerize spontaneously to resins. Grignard and Lapayre<sup>145</sup> found that 1-phenylpenta-4-ene-1-yne,  $C_6H_5-C\equiv C-CH_2-CH=CH_2$ , resinifies on standing.

Hydrocarbons thought to be



were obtained by Lespieau and Journaud.<sup>146</sup> These hydrocarbons were formed by the action of allyl iodide on monosodium acetylide. When heated, they slowly polymerized. Likewise the pyrolysis of the methyl-substituted propargylphenyl ethers.



gave resins and tars.<sup>147</sup>

<sup>138</sup> S. Skraup and E. Beng, *Ber.*, 1927, 60, 945; *Chem. Abs.*, 1927, 21, 2125.

<sup>139</sup> K. Krasousky and A. Kiprianov, *J. Russ. Phys.-Chem. Soc.*, 1925, 56, 1; *Chem. Abs.*, 1925, 19, 2817.

<sup>140</sup> A. F. Hunt and E. E. Turner, *J.C.S.*, 1925, 127 (1), 998.

<sup>141</sup> F. G. Müller, *Helv. Chim. Acta*, 1925, 8, 826; *Chem. Abs.*, 1926, 20, 1051.

<sup>142</sup> F. Straus, L. Kollek and H. Hauptmann, *Ber.*, 1930, 63, 1886; *Chem. Abs.*, 1931, 25, 73.

<sup>143</sup> F. Straus and L. Kollek, *Ber.*, 1926, 59, 1664; *Chem. Abs.*, 1927, 21, 50.

<sup>144</sup> L. Henry, *Ber.*, 1881, 14, 401; *Chem. Zentr.*, 1881, 308.

<sup>145</sup> V. Grignard and L. Lapayre, *Compt. rend.*, 1931, 192, 250; *Chem. Abs.*, 1931, 25, 2421.

<sup>146</sup> R. Lespieau and Journaud, *Bull. soc. chim.*, 1931, (4) 49, 423; *Brit. Chem. Abs.*, A, 1931, 709.

<sup>147</sup> C. D. Hurd and F. L. Cohen, *J.A.C.S.*, 1931, 53, 1068.

Tolane (diphenylacetylene) heated with 4,5-diphenylcyclopentenolone (anhydro-acetone-benzil) yielded a small amount of colorless crystals (m. p. 262-263°C) of tetraphenyl-benzene, together with a larger quantity of a resinous body.<sup>148</sup> Formation of the latter was reduced by carrying out the reaction in the absence of air.

<sup>148</sup> W. Diltley and G. Hurtig, *Ber*, 1934, 67, 2004.

## Chapter 9

# Polymerization of Hydrocarbon Olefins and Diolefins. Synthetic Rubber

The part played by polymerization in resin-forming reactions has already been discussed in Chapter 4. The present chapter deals solely with polymerization reactions involving unsaturated aliphatic and alicyclic hydrocarbons.<sup>1</sup> These compounds, as a class, including monolefins, diolefins and acetylenes,<sup>2</sup> possess an inherent tendency to polymerize. This tendency is not exhibited by typical saturated hydrocarbons, e.g., paraffins and cycloparaffins, nor by aromatic hydrocarbons.

Simple monolefins of the type  $R^1R^2C=CR^3R^4$ , in which  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are hydrogen atoms or alkyl groups, are capable of undergoing additive polymerization under the influence of heat, catalysts, the silent electric discharge, alpha-radiation, ultraviolet light, and similar energizing influences, but in most cases the products of such polymerization reactions are oily rather than resinous. The tendency of monolefins to undergo polymerization is greatly increased by the introduction of an electronegative group into the molecule at one of the carbon atoms in the ethylenic grouping. Accordingly, the so-called vinyl compounds (i.e. compounds of the type  $CH_2CX$ , where  $X$  is an electronegative atom or group), including styrene, vinylnaphthalene, vinyl halides, vinyl ethers and vinyl esters (see Chapters 11 and 51-53) are capable of undergoing very rapid polymerization, particularly in the presence of catalysts, with the formation of macromolecules possessing resinous characteristics.

In contrast to these readily polymerizable, negatively substituted olefins, the simple ethylene homologues are polymerized less easily and do not tend to form products of very high molecular weight except, perhaps, under very special circumstances. Thermal treatment of ethylene and its homologues has been found to yield simple polymers (the polymers themselves being olefins of double or treble the molecular weight of the parent hydrocarbon) but so many other reactions occur simultaneously that the true polymers are always present with other substances. At temperatures above 650°C. the main products of the pyrolysis of olefins are aromatic hydrocarbons and tars.

Since in most cases the monolefins yield only oily polymers, the diolefins are of more interest in the present discussion. Consequently the greater part of the chapter deals with the polymerization of the latter type of compound. Considerable study has been devoted to diolefins (particularly those containing conjugated double bonds) toward their conversion into products of high molecular weight. The object in view has been the production of a material which will meet the requirements demanded of a substance designed to replace natural rubber.

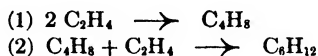
### POLYMERIZATION OF MONOLEFINS

Resinous substances, as well as oils, have been obtained by polymerization of the lower monolefins under the activating influence of the silent discharge. These

<sup>1</sup> Cf. the discussion of this subject by Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934.

<sup>2</sup> The polymerization of acetylene and its homologues and derivatives is treated in Chapter 8.

resinous products, however, are probably not true polymers of the original olefin but are formed as a result of a series of splitting and polymerization steps. By subjecting ethylene to a silent electrical discharge at  $-20^{\circ}\text{C}$ . for two weeks, Collie<sup>3</sup> obtained 10 grams of a product which boiled from below  $100^{\circ}\text{C}$ . to  $250^{\circ}$  and left a rubber-like residue. The latter had a composition closely agreeing with  $(\text{C}_6\text{H}_8)_x$ . An explanation of the mechanism of the initial polymerization reaction of ethylene in the presence of a high-frequency electric discharge is offered by Mignonac and Vanier de Saint-Aunay.<sup>4</sup> By circulating ethylene through the discharge at  $0-10^{\circ}\text{C}$ . and subsequently through a condenser cooled to  $-60^{\circ}$ , they were successful in polymerizing 90-95 per cent of the olefin. The product was found to be essentially a mixture of 1-butene and 1-hexene. The yield of 1-butene was greatly increased by cooling the condenser to  $-80^{\circ}$  and circulating the gas more slowly. By raising the condenser temperature, the product consisted essentially of 1-hexene. It would seem then, that two consecutive reactions were taking place.



These results were confirmed by Szukiewicz<sup>5</sup> who also experimented with a lower power discharge to obtain, among other hydrocarbons, butene, 1,3-butadiene and acetylene. Other investigators have noticed that hydrogen and methane as well as additional saturated hydrocarbons are simultaneously produced, so that a complex reaction mechanism must be postulated. In the products of the action of the silent discharge on isobutylene, Pryanischnikov and Demijanov<sup>6</sup> found both saturated and unsaturated hydrocarbons of varying degrees of molecular complexity. On prolonged exposure to the discharge, resinous substances of high molecular weight were formed, probably by fission and further polymerization. Upon subjecting trimethylethylene to the influence of a silent discharge, Losanitsch<sup>7</sup> obtained a brownish-yellow mass of the composition  $\text{C}_{10}\text{H}_{16}$  [i.e.,  $(\text{C}_5\text{H}_{10})_2 - 7\text{H}_2$ ] as well as colorless, liquid "diamylene" and "tetra-amylenes." In view of the nature of the resinous products it appears not unlikely that they are formed from diolefinic substances, produced by dehydrogenation of the simple olefinic polymers. By the action of a semi-corona discharge on various gases, including ethylene, Lind and Glockler<sup>8</sup> obtained considerable quantities of a resinous or gummy solid which was inert towards solvents and chemical reagents, except strong oxidizing agents. Exposure of 193 grams of ethylene to a discharge of 18,000 volts for 12.4 days gave 78.6 g. of this resinous solid and 40.1 g. of liquid condensation products.<sup>9</sup> Subjection of lower olefins to alpha-radiation and other energizing influences gives liquid and resinous condensation products similar to those obtained with the silent discharge.<sup>10</sup>

A number of catalysts are very active in promoting the polymerization of ethylene and its homologues to substances of varying degrees of molecular com-

<sup>3</sup> J. N. Collie, *J.C.S.*, 1905, 87, 1340; *Proc. Chem. Soc.*, 1905, 21, 201; *J.S.C.I.*, 1905, 24, 818. See also M. P. E. Berthelot, *Compt. Rend.*, 1896, 126, 567; *J.C.S.*, 1898, 74, (1), 393.

<sup>4</sup> G. Mignonac and R. Vanier de Saint-Aunay, *Compt. Rend.*, 1929, 189, 106; *Chem. Abs.*, 1929, 23, 4668. Cf. R. Vanier de Saint-Aunay, *Chimie et Industrie*, 1933, 29, 1011; *Chem. Abs.*, 1933, 27, 3911.

<sup>5</sup> W. Szukiewicz, *Roczniki Chem.*, 1933, 13, 245 (in English 255); *Chem. Abs.*, 1933, 27, 4487.

<sup>6</sup> N. Y. Pryanischnikov and N. D. Demijanov, *J. Russ. Phys.-Chem. Soc.*, 1926, 58, 462; *Chem. Abs.*, 1927, 21, 3344. N. Y. Pryanischnikov, *Ber.*, 1928, 61, 1558; *Chem. Abs.*, 1928, 22, 4453.

<sup>7</sup> S. M. Losanitsch, *Bull. soc. chim. Bucharest*, 1914, 23, 3; *Chem. Abs.*, 1917, 11, 254.

<sup>8</sup> S. C. Lind and G. Glockler, *J.A.C.S.*, 1929, 51, 2818.

<sup>9</sup> For polymerisation of products from gases containing methane, ethylene and acetylene when subjected to high-frequency oscillations at temperatures above  $900^{\circ}\text{C}$ ., see British P. 355,210, 1929, to Ruhrehernie A.-G.; *Chem. Abs.*, 1932, 26, 4085.

<sup>10</sup> W. Mund and W. Koch, *Bull. soc. chim. Belg.*, 1925, 34, 125, 241; *Chem. Abs.*, 1925, 19, 1986.

plexity. Among the more important catalysts, the following may be mentioned: concentrated sulphuric acid, hydrogen fluoride, ozone,<sup>11</sup> aluminum chloride,<sup>12</sup> boron trifluoride, zinc chloride, stannic chloride, activated hydrosilicates such as floridin, and anhydrous metallic halides activated by the addition of finely divided metals. The products of reaction consist of oils ranging from volatile liquids to viscous syrups. Low temperatures favor the formation of very high-molecular-weight materials. The high-boiling oily polymerization products obtained under the influence of aluminum chloride and boron trifluoride have been suggested as lubricating oils.<sup>13</sup> Brown, viscous and sticky liquids were obtained by Stanley<sup>14</sup> by the polymerization of ethylene under pressure in the presence of aluminum chloride at 0-10°C. and these possessed molecular weights represented by the formula  $(C_2H_4)_x$ , where x was as high as 40 or 50. Monolefins have been polymerized to yield products of high molecular weight by using inorganic volatile halides as catalysts.<sup>15</sup> For example, boron fluoride may be bubbled through isobutylene cooled to -80°C. Additional catalysts, prepared by charging boron fluoride with hydrogen fluoride, phosphorus tri- or pentafluorides and aluminum chloride have been recommended. According to Waterman, Over and Tulleners,<sup>16</sup> the polymerization of isobutylene, catalyzed by aluminum chloride, is violent and sometimes even explosive when carried out at -78°C. Under these conditions a pale-yellow polymerization product was isolated whose molecular weight was estimated at 600-700. The polymer is described as very tough and sticky with a capacity for being drawn into threads. An interesting polymerizing agent is floridin (or Florida earth), since this material appears to polymerize the lower olefins to a complex mixture of liquids, which still contain a double bond of unsaturation. In the presence of floridin, isobutylene<sup>17</sup> polymerizes even at -80°C., but more rapidly at room temperature, to yield a mixture of polymers, some of which are very viscous and of high molecular weight. Thus, 71 per cent of the polymers obtained by bringing isobutylene in contact with floridin at room temperature boiled above 185°. Staudinger and Brunner<sup>18</sup> have examined isobutylene polymerized in the presence of floridin, first at -80°C. and then at 5°C. They separated the resulting mixture, by distillation and subsequent extraction with alcohol, into triisobutylene, pentaisobutylene, and a polyisobutylene. The latter was subsequently purified by precipitation from an ethereal solution by the addition of alcohol. The product, so obtained, was a viscous mass with a density 0.9 and a mean molecular weight of 1600 in benzene. The material was stable toward warm potassium permanganate and nitric acid but absorbed bromine to the extent of 50 per cent of

<sup>11</sup> Ozone reacts with ethylene hydrocarbons forming ozonides which readily polymerize in some cases to solid gummy or glassy substances. The explosive character of ozonides is such as to deter usage in the synthetic resin field. The subject of ozonides has been summarized by C. D. Harries, *Ann.*, 1905, 343, 311; 1910, 374, 283; 1913, 390, 236; 1915, 410, 1; *Chem. Abs.*, 1910, 4, 2633; 1912, 6, 2154; 1915, 9, 2877. See also R. Koetschau, *Z. angew. Chem.*, 1922, 35, 509; *Chem. Abs.*, 1923, 17, 337. For investigations on the polymerization of isobutene and of pentenes using aluminum chloride as catalyst see H. I. Waterman, J. J. Leendertse and A. J. de Kok, *Rec. trav. chim.*, 1934, 53, 1151. H. I. Waterman, J. J. Leendertse and W. M. Klazinga, *ibid.*, 1935, 54, 79. H. I. Waterman and J. J. Leendertse, *ibid.*, 1935, 54, 139.

<sup>12</sup> French P. 680,038, 1929, to Pure Oil Co.; *Chem. Abs.*, 1930, 24, 3799. C. Engler and O. Routsala (*Ber.*, 1909, 42, 4610, 4613; *Chem. Abs.*, 1910, 4, 767) found that anhydrous aluminum chloride converted anylene into a heavy oil, whereas ethylene and terpenes are polymerized to balsam-like products.

<sup>13</sup> F. W. Sullivan, V. Voorhees, A. W. Neeley and R. V. Shankland, *Ind. Eng. Chem.*, 1931, 23, 604. A. W. Nash, H. M. Stanley and A. R. Bowen, *J. Inst. Pet. Tech.*, 1930, 16, 830. M. Otto, *Brennstoff-Chem.*, 1927, 8, 321. Krauch, *Proc. 2nd Intern. Conference Bituminous Coal*, 1928, 1, 32.

<sup>14</sup> H. Stanley, *J.S.C.I.*, 1930, 49, 349T. W. H. Hunter and R. V. Yohe, *J.A.C.S.*, 1933, 55, 1248.

<sup>15</sup> British P. 401,297, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2307.

<sup>16</sup> H. I. Waterman, J. Over and A. J. Tulleners, *Rec. trav. chim.*, 1934, 53, 699; *Chem. Abs.*, 1934, 28, 5397.

<sup>17</sup> S. V. Lebedev and G. G. Kobliansky, *Ber.*, 1930, 63, 103, 1432; *Chem. Abs.*, 1930, 22, 4255. S. V. Lebedev and E. P. Filonenko, *Ber.*, 1925, 58, 163; *Chem. Abs.*, 1925, 19, 1555. S. V. Lebedev and J. M. Slobodin, *J. Gen. Chem. Russia*, 1934, 4, 23; *Brit. Chem. Abs.*, A, 1934, 864.

<sup>18</sup> H. Staudinger and M. Brunner, *Helv. Chim. Acta*, 1930, 13, 1375; *Chem. Abs.*, 1931, 25, 3519.

the theoretical amount for one double bond, in  $(C_6H_8)_n$ . Its solubility, viscosity, and physical properties were very similar to those of a hemicolloidal hydorrubber, obtained by the hydrogenation of natural rubber or rubber latex. (See Chapter 54.)

Sulphuric acid converts many of the simple monolefins to only polymers but it also exerts a splitting action on these polymers so that both saturated and highly unsaturated hydrocarbons are formed.<sup>19</sup> None of the simple monolefins give rise to resinous substances similar to the products formed from vinyl compounds, cumarone or indene under the influence of concentrated sulphuric acid. According to Friese,<sup>20</sup> however, cyclohexene and concentrated sulphuric acid react vigorously to form a dark resin, insoluble in water. A resinous product was obtained by Nametkin and Abakumovskaja<sup>21</sup> by reaction of cooled sulphuric acid (sp. gr. 1.84) on one-third of its volume of cyclohexene.<sup>22</sup> Isobutylene, trimethylethylene and similar monolefins are converted into their simple di- and trimers by treatment with sulphuric acid of about 80 per cent concentration, or even lower.<sup>23</sup> However viscous or solid polymers of high molecular weight are obtained by the action of liquid sulphur dioxide on isobutylene.<sup>24</sup> The reaction is carried out in sealed tubes and catalyzed by sunlight to yield compounds having the empirical composition  $(C_4H_8SO)_x$ . Propylene and amylene are said to give solid polymers under similar conditions.

Zelinsky and Borisov<sup>25</sup> treated cyclohexene with oxygen in the absence of catalyst for 151 days and obtained, after removal of unchanged cyclohexene, a resinous reddish-yellow mass, which analysis showed to be the peroxide. However, the constitution of the resinous substance is not known. Studies on the polymerization of cyclohexene have been made by Waterman and co-workers.<sup>26</sup> With pentane as a liquid diluent and aluminum chloride as catalyst polymerization was only slight at 40°C. However, at 70°, treatment with 6-7 per cent aluminum chloride for 7 hours resulted in more than 50 per cent conversion of cyclohexene into high-molecular oily compounds. Although at -78°C. cyclohexene exhibited practically no polymerization in the presence of pentane and aluminum chloride, the simultaneous addition of hydrochloric acid and aluminum chloride under these conditions resulted in a rapid reaction, yielding monochlorocyclohexane and a mixture of monochloro-polycyclohexyl compounds.

The effect of sulphur dioxide upon the polymerization of cyclohexene has been investigated by Marvel, Frederick and Cogan.<sup>27</sup> The product obtained by allowing cyclohexene, liquid sulphur dioxide and an oxidizing catalyst to stand in a pressure flask at room temperature is a hard, brittle, white, amorphous solid. The degradation products obtained by treating this substance with non aqueous alkali indicate that it is a polymeric sulphone whose most probable structure is

<sup>19</sup> W. R. Ormandy and E. C. Craven, *J. Inst. Pet. Tech.*, 1927, 13, 844; *J.S.C.I.*, 1928, 47, 317T; 1929, 48, 293T.

<sup>20</sup> H. Friese, *Ber.*, 1931, 64, 2103, *Brit. Chem. Abs. A*, 1931, 1286.

<sup>21</sup> S. Nametkin and L. Abakumovskaja, *Ber.*, 1933, 66, 358; *Chem. Abs.*, 1933, 27, 2677; *J. Gen. Chem. Russia*, 1932, 2, 608; *Brit. Chem. Abs.*, A, 1933, 152.

<sup>22</sup> Cyclohexene condenses with benzyl alcohol in the presence of phosphorus pentoxide to form 1-benzylcyclohexene and much tarry matter. D. N. Kursanov, *J. Russ. Phys.-Chem. Soc.*, 1930, 62, 1691, *Chem. Abs.*, 1931, 25, 2698.

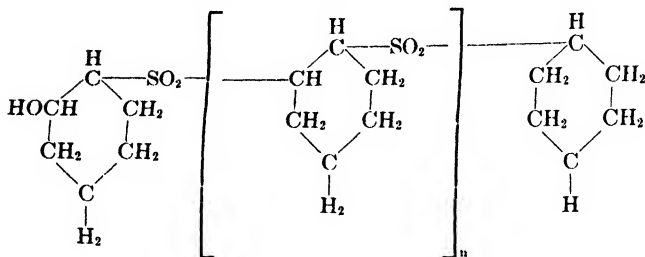
<sup>23</sup> A. Butlerow, *Ber.*, 1879, 12, 1482; *J.C.S.*, 1880, 38, 230. W. von Schneider, *Ann.*, 1871, 157, 185, 207; *Chem. Zentr.*, 1871, 1, 2. J. F. Norris and J. M. Joubert, *J.A.C.S.*, 1927, 49, 873. B. T. Brooks and I. Humphrey, *J.A.C.S.*, 1918, 40, 822. See also French P. 737,743, 1932, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, 27, 1638.

<sup>24</sup> F. E. Matthews and H. M. Elder, British P. 11,635, 1914; *Chem. Abs.*, 1915, 9, 2971.

<sup>25</sup> N. D. Zelinsky and P. P. Borisov, *Ber.*, 1930, 63, 2362; *J. Russ. Phys.-Chem. Soc.*, 1930, 62, 2051; *Chem. Abs.*, 1931, 25, 2044. See also H. N. Stevens, *Ber.*, 1931, 64, 637; *Chem. Abs.*, 1931, 25, 397.

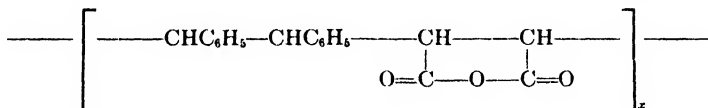
<sup>26</sup> H. I. Waterman, J. J. Leendertse and A. C. ter Poorten, *Rac. trav. chim.*, 1935, 54, 245.

<sup>27</sup> C. S. Marvel, D. S. Frederick and H. D. Cogan, *J.A.C.S.*, 1934, 56, 1815.



A halogen-containing derivative can be prepared by treating the polysulphone with chloroacetyl chloride. Halogen analyses and molecular-weight determinations carried out with the derivative indicate that the value of  $n$ , in the above formula, is about 39. Experiments<sup>28</sup> carried out at  $-30^\circ\text{C}$ . with cyclohexane and sulphur dioxide in the presence of oxygen yielded a polymer with the approximate formula  $(\text{C}_6\text{H}_9\text{SO}_2)_x$ . When no oxygen was used the material obtained had the formula  $(\text{C}_6\text{H}_8\text{SO}_2)_x$ .

Resinous and gummy polymerization products have been obtained from monolefins by Wagner-Jauregg's<sup>29</sup> so-called "additive heteropolymerization" process in which two unlike units of low molecular weight and containing ethylene linkages may undergo addition and polymerization simultaneously. In this type of reaction maleic anhydride, which has no tendency to polymerize but which shows a marked additive capacity, has been used exclusively as a constant member of such mixtures. When sym-diphenylethylene and maleic anhydride are boiled in xylene, a white amorphous, infusible substance is formed. The examination of the resin would seem to indicate a product composed of definite units, such as



in which  $x$  corresponds to an average of 15.

Viscous, gummy polymers resulted when anilene and styrene were heated with maleic anhydride. (See Chapters 11 and 40). In general, it may be said that the nature of substituent groups, proper selection of solvents, and steric hindrance affect the ease of heteropolymerization.

#### POLYMERIZATION OF DIOLEFIN HYDROCARBONS

Of the diolefin hydrocarbons, only those containing a conjugated system of double bonds and including butadiene and its homologues as well as cyclic diolefins of the type of cyclopentadiene, need be considered. These conjugated diolefins exhibit a very pronounced tendency to polymerize to resinous or rubber-like polymers, as well as to lower liquid polymers, under a wide variety of influences. Other diolefinic hydrocarbons including 1,2-diolefins (or allenes), 1,4-, 1,5-, and 1,6-diolefins do not polymerize so readily or as profoundly as the conjugated dienes.

In the polymerization of butadiene and its simple homologues, products of widely varying properties are obtained depending upon the experimental conditions. Besides liquid cyclic dimers and trimers, the high-molecular-weight amor-

<sup>28</sup> W. F. Seyer and E. G. King, *J.A.C.S.*, 1933, 55, 3140.

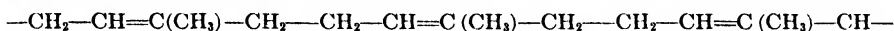
<sup>29</sup> T. Wagner-Jauregg, *Ber.*, 1930, 63, 3213; *Chem. Abs.*, 1931, 25, 2418.



phous polymers, simultaneously formed, may be roughly separated into several qualitatively different species of polymeric mixtures.

The aim of all endeavors to polymerize conjugated diolefins to high-molecular-weight polymers has been the production of a synthetic rubber capable of meeting all the complex technical requirements of natural rubber, particularly the ability to be vulcanized. In spite of nearly half a century of scientific and industrial investigation in this field, the problem of the successful synthesis of true rubber on a technical scale is still unsolved. For special purposes, however, the synthetic rubber-like polymers of the conjugated diolefins may find industrial application.

**Polymerization of Butadiene and Its Homologues.** Natural rubber is supposed to consist of a mixture of polymeric hydrocarbons whose general configuration can be written.<sup>30</sup>



The rubber molecule consists, therefore, of a long chain of units composed of many hundreds of isoprene molecules  $\begin{array}{c} \text{CH}_2=\text{C}-\text{CH}=\text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$  combined by a process of

1,4-addition.<sup>31</sup> Accordingly the most obvious raw material for conversion into rubber-like substances by polymerization is isoprene itself. Isoprene possesses an unusual tendency to polymerize and in fact was the first conjugated diolefin to be transformed into a rubber-like material.<sup>32</sup>

However, it is by no means the only hydrocarbon of this type capable of undergoing such polymerization. Both butadiene<sup>33</sup> and 2,3-dimethylbutadiene<sup>34</sup> were found to polymerize under the influence of heat and catalysts but not quite so readily as isoprene. Although the data available on the extent to which the tendency of butadiene homologues to polymerize to rubber-like and resinous polymers are far from complete, certain facts are now well established. Of the butadiene homologues containing one methyl group, both 1- and 2-methylbutadienes (piperylene and isoprene) are polymerizable to caoutchouc-like substances; but, of the disubstituted members, only 2,3- and 1,4-dimethylbutadienes undergo this condensation. Fisher and Chittenden<sup>35</sup> encountered difficulty in polymerizing 1,2-dimethylbutadiene on account of the slowness of reaction. According to the observation of Kyriakides,<sup>36</sup> the 1,1-dimethyl compound is polymerizable, although Harries<sup>37</sup> states that the change occurs only with difficulty. Furthermore, 1,2,3,4-tetramethylbutadiene shows no tendency to polymerize.<sup>38</sup> It appears that methyl substituents in butadiene diminish the ease of polymerization and that methyl substitution in the terminal positions has a more unfavorable effect on polymerization tendency than substitution in the middle positions.<sup>39</sup> The intro-

<sup>30</sup> Thermal decomposition of natural and butadiene rubber, at lower temperatures than in the ordinary cracking process and catalyzed by aluminum chloride, yields a gasoline-like fluid high in aromatic compounds. In neither instance was isoprene obtained. This may indicate the formation of aromatic compounds during the polymerization of butadiene hydrocarbons. N. D. Zelinski and N. S. Kozlov, *J. Applied Chem. (U. S. S. R.)*, 1933, 6, 36; *Chem. Abs.*, 1933, 27, 6015. *Rubber Chem. Tech.*, 1933, 6, 64; *Chem. Abs.*, 1933, 27, 6013.

<sup>31</sup> A discussion of the constitution of rubber is given by D. K. Memmler, "The Science of Rubber" English translation by R. F. Dunbrook and V. N. Morris, Chemical Catalog Co., New York, 1934.

<sup>32</sup> G. Boucardat, *Compt. rend.*, 1879, 89, 1117; *J.C.S.*, 1880, 38, 323. W. A. Tilden, *Chem. News*, 1882, 46, 120; *J.C.S.*, 1883, 44, 75.

<sup>33</sup> C. D. Harries, *Ann.*, 1911, 383, 157; *Chem. Abs.*, 1911, 5, 3519.

<sup>34</sup> I. L. Kondakov, *J. prakt. Chem.*, 1901, 64, 109; *J.C.S.*, 1901, 80, (1), 625.

<sup>35</sup> H. L. Fisher and F. D. Chittenden, *Ind. Eng. Chem.*, 1930, 22, 869.

<sup>36</sup> I. P. Kyriakides, *J.A.C.S.*, 1914, 36, 987.

<sup>37</sup> C. D. Harries, "Untersuchungen über die natürlichen und künstlichen Kautschukarten," Julius Springer, Berlin, 1919, 250.

<sup>38</sup> A. D. Macallum and G. S. Whitby, *Trans. Roy. Soc. Canada*, 1928, 22 (3), 39; *Brit. Chem. Abs.*, A, 1928, 614.

<sup>39</sup> The velocity of polymerization of various diolefins is discussed by E. M. Gapon, *J. Russ. Phys.-Chem. Soc.*, 1930, 62, 1385; *Chem. Abs.*, 1931, 25, 2968; *J. Gen. Chem. (Russia)*, 1931, 1, 496, 765, 779;

duction of phenyl groups into the butadiene system is said by Whitby and Gallay<sup>40</sup> to favor the formation of dimers but to inhibit further polymerization.<sup>41</sup> However, the polymerization does not stop at the dimer stage if the proper catalysts are employed. Staudinger and Ashdown,<sup>42</sup> using stannic chloride as a catalyst, were able to prepare polymers of 1-phenylbutadiene having an approximate molecular weight of 1500. Benzene or carbon tetrachloride is an appropriate solvent for the reaction.

The substitution of a halogen for a hydrogen atom in the butadiene system has given very interesting results. 2-Chlorobutadiene, or chloroprene, on standing undergoes complete transformation to rubber-like polymers in a few days, while 2-bromobutadiene polymerizes even more rapidly.<sup>43</sup> The ease and nature of polymerization depends not only upon the presence of halogen, but also upon its position in the molecule. For example, Staudinger<sup>44</sup> and his co-workers found that mixtures of monobromoisoprenes, obtained by treating 1,4-dibromo-2-methyl-2-butene with sodium methoxide, would not polymerize in the cold and decomposed when heated. Similarly a dibromoisoprene (b. p. 78-83°C. at 12 mm.), produced by splitting out of 2 molecules of hydrogen bromide from isoprene tetrabromide, decomposed upon heating instead of polymerizing. Muscat and Northrup<sup>45</sup> reported a dark resinous mass from the polymerization of 1-chlorobutadiene.

Resinous products resembling rubber or celluloid and capable of being rolled into thin sheets have been obtained by the polymerization of dichlorobutadiene.<sup>46</sup> The latter is made by splitting off 2 mols of hydrochloric acid from tetrachlorobutane with alcoholic potash. The polymerization is carried out in a closed vessel at 20-50°C., oxygen being excluded. Insolubility in benzene is imparted to the final product by a heat treatment at 140-150° for 10 minutes.

In the polymerization of butadiene and its homologues, several types of polymers are formed depending on the conditions. These include liquid dimers and trimers, pasty or plastic polymers, tough rubber-like substances, and also granular masses. There is some disagreement among different investigators as to the exact nature of the dimer formed, although it is believed that the product is a monocyclic compound. Experiments dealing with the thermal polymerization of isoprene have indicated that the mechanism of the reaction is essentially a bimolecular association process.<sup>47</sup> However, regarding the higher polymers, the constitution is still quite obscure. In the preparation of synthetic rubber, the liquid polymers contaminate the product and may be removed by treating the mass with such powdered absorbents as activated carbon or silicon dioxide.<sup>48</sup> The constitution of the synthetic-rubber polymers is still unclarified.

The influence of structural modifications on the polymerization of butadiene derivatives with respect to rate of polymerization and the character of the polymers formed is summarized in Table 22.

*Chem. Abs.*, 1932, 26, 4590; *Brit. Chem. Abs.*, A, 1932, 232. See also N. D. Zelinski, Y. I. Denisenko, M. S. Eventova and S. I. Khromov, *Smet. Kauchuk*, 1933, 4, 11; *Brit. Chem. Abs.*, A, 1934, 1080.

<sup>40</sup> G. S. Whitby and W. Gallay, *Can. J. Research*, 1932, 6, 280; *Brit. Chem. Abs.*, A, 1932, 496. See also I. E. Muskat and M. Herrmann, *J. A.C.S.*, 1931, 53, 252.

<sup>41</sup> A. Mironescu, G. Ioanid and L. Nicolaeu (*Bull. Soc. Chim. Romania*, 1932, 14, 187; *Chem. Abs.*, 1933, 27, 4231) also report that difurylbutadiene is a remarkably stable compound.

<sup>42</sup> H. Staudinger and A. A. Ashdown, *Ber.*, 1930, 63, 717; *Chem. Abs.*, 1930, 24, 5716.

<sup>43</sup> W. H. Carothers, I. Williams, A. M. Collins and J. E. Kirby, *J. A.C.S.*, 1934, 53, 4203. See Chapter 8.

<sup>44</sup> H. Staudinger, O. Muntwyler, and O. Kupfer, *Helv. Chim. Acta*, 1922, 5, 756; *Chem. Abs.*, 1923, 17, 2974.

<sup>45</sup> I. E. Muscat and H. E. Northrup, *J. A.C.S.*, 1930, 52, 4046.

<sup>46</sup> British P. 413,469, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2264. French P. 772,189, 1934; *Chem. Abs.*, 1935, 29, 1541.

<sup>47</sup> W. E. Vaughan, *J. A.C.S.*, 1933, 55, 4109.

<sup>48</sup> C. Meisenburg, German P. 511,540, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1705.

TABLE 22.—Relative Polymerization Speeds of Various Dienes at 25 °C. Compared with Isoprene.\*

Compound	Estd. Speed*	Character of Polymer
$\text{H}_2\text{C}=\text{CCl}-\text{CCl}=\text{CH}_2^{\circ}$	2000	Hard, not extensible
$\text{H}_2\text{C}=\text{Cl}-\text{CH}=\text{CH}_2^{\dagger}$	1500	Rubber-like under certain conditions
$\text{H}_2\text{C}=\text{CBr}-\text{CH}=\text{CH}_2^{\ddagger}$	1000	Good rubber
$\text{H}_2\text{C}=\text{CCl}-\text{CH}=\text{CH}_2^b$	700	Excellent rubber
$\text{H}_2\text{C}=\text{CCl}-\text{C}(\text{CH}_3)=\text{CH}_2^{\dagger}$	500	Fair rubber but low extensibility
$\text{HCCl}=\text{CCl}-\text{CCl}=\text{CH}_2^{\circ}$	120	Soft, elastic
$\text{H}_2\text{C}=\text{C}(\text{C}_6\text{H}_5)-\text{CH}=\text{CH}_2^k$	90	Soft
$\text{HC}(\text{CH}_3)=\text{CCl}-\text{CH}=\text{CH}_2^m$	30	Soft
$\text{HC}(\text{C}_6\text{H}_5)=\text{CCl}-\text{CH}=\text{CH}_2$	30	Soft
$\text{HC}(\text{C}_6\text{H}_5)=\text{CCl}-\text{CH}=\text{CH}_2$	10	Soft
$\text{HC}(\text{C}_7\text{H}_{15})=\text{CCl}-\text{CH}=\text{CH}_2^m$	10	Soft
$\text{H}_2\text{C}=\text{C}(\text{C}_7\text{H}_{15})-\text{CH}=\text{CH}_2^k$	9	Soft
$\text{HCCl}=\text{CH}-\text{CH}=\text{CH}_2$	7	Soft, sticky
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}_2^b$	3	Fair rubber but low extensibility
$\text{HC}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{CCl}=\text{CH}_2^{\dagger}$	1.5	Soft
$\text{H}_2\text{C}=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2^b$	1.0	Fair rubber
$\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$	0.8	Fair rubber
$\text{HC}(\text{CH}_3)=\text{CH}-\text{CH}=\text{CH}_2^c$	0.3	..
$\text{HC}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2^d$	Probably	..
	<1	..
$(\text{H}_3\text{C})_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2^d$		
$\text{HC}(\text{CH}_3)=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2^d$		
$\text{HC}(\text{CH}_3)=\text{CH}-\text{CH}=\text{CH}(\text{CH}_3)^d$		
$(\text{H}_3\text{C})_2\text{C}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2^d$		
$(\text{H}_3\text{C})_2\text{C}=\text{CH}-\text{CH}=\text{CH}(\text{CH}_3)^d$		
$\text{HC}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{C}(\text{CH}_3)=\text{CH}(\text{CH}_3)^d$		
$(\text{H}_3\text{C})_2\text{C}=\text{CH}-\text{CH}=\text{C}(\text{CH}_3)^d$		

\* W. H. Carothers, *Ind. Eng. Chem.*, 1934, 26, 30.

The estimated speeds are based on calculated unimolecular reaction velocity constants. The data from which the constants are derived suffer from a very large factor of uncertainty owing to the fact that, for dienes, the rate of polymerization varies considerably with the history of the sample and with conditions (amount of exposure to light and air) which are not specified or controlled in all of the experiments. These uncertainties are, however, thought to be insufficient to affect the order of magnitude of the indicated numbers.

<sup>b</sup> The constant taken for isoprene was 0.0000048 (in hours) and was derived, by extrapolation, from data presented by G. S. Whitby and R. N. Crozier, *Can. J. Research*, 1932, 6, 203; *Brit. Chem. Abs.* A, 1932, 361.

<sup>c</sup> Data of S. V. Lebedev and B. K. Mereshkovski quoted by G. S. Whitby and W. Gallay, *Can. J. Research*, 1932, 6, 280; *Chem. Abs.*, 1932, 26, 3479.

<sup>d</sup> G. S. Whitby and W. Gallay, *loc. cit.*

<sup>e</sup> G. J. Berechet and W. H. Carothers, *J. A. C. S.*, 1933, 55, 2004.

<sup>f</sup> W. H. Carothers and G. J. Berechet, *ibid.*, 1933, 55, 2807.

<sup>g</sup> W. H. Carothers, A. M. Collins and J. E. Kirby, *ibid.*, 1933, 55, 786.

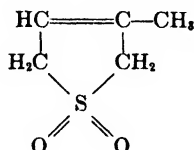
<sup>h</sup> W. H. Carothers, I. Williams, A. M. Collins and J. E. Kirby, *ibid.*, 1931, 53, 4203.

<sup>i</sup> W. H. Carothers and D. D. Coffman, *ibid.*, 1932, 54, 4071.

<sup>j</sup> W. H. Carothers and G. J. Berechet, *ibid.*, 1933, 55, 2813.

<sup>k</sup> R. A. Jacobson and W. H. Carothers, *ibid.*, 1933, 55, 1822.

**Butadiene Sulphones.** By treating isoprene in an ethereal solution with sulphur dioxide,<sup>40</sup> crystalline isoprene sulphone, melting at 63-63.5°C., may be obtained in a yield of 60 per cent. The following constitution has been assigned to the compound:



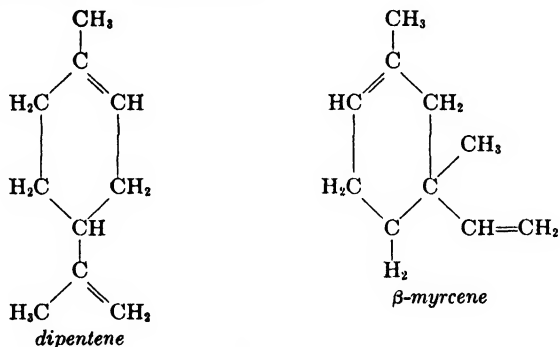
Isoprene sulphone readily takes up bromine (in carbon tetrachloride) to form the dibromide melting at 127°C. Upon treating the dibromide with sodium hydroxide in a methyl alcohol solution, a polymer of 2-methyl-2,3-butadiene

<sup>40</sup> E. Eigenberger, *J. prakt. Chem.*, 1930, 127, 307; *Chem. Abs.*, 1931, 25, 276.

sulphone  $<1,4>$  is formed. The allene nature of the polymer was assumed from its degradation products and because of its ease of oxidation and general unsaturated nature except towards bromine. Subsequently Eigenberger<sup>50</sup> found that when isoprene sulphone was treated with dilute aqueous or alcoholic potassium hydroxide in the light of a quartz lamp, an isomeric isoprene sulphone B, melting at 79°C., could be recovered. The alkali is an essential factor, for the reaction will not take place in the presence of the radiation alone. Isoprene sulphone gave, upon treatment with potassium in dry ether, the potassium salt of 3,6-dimethyl-2,4-octadiene-1,8-disulphinic acid. The product was characterized by its pronounced instability and tendency toward polymerization. The polymerization product, in this case, was an ether-insoluble, amorphous compound, soluble in ethyl acetate.

**Liquid or Oily Polymers.** Liquid polymers are produced from butadiene hydrocarbons under a variety of circumstances but usually under the influence of heat and in the absence of active polymerizing agents. Most of these liquid polymers are cyclic unsaturated hydrocarbons and are by-products of the rubber syntheses, i.e., they cannot be polymerized further to rubber-like substances. However, the dimers of 2,3-dimethylbutadiene are polymerized rapidly in the cold under the influence of antimony pentachloride or stannic chloride, yielding high-molecular-weight polymers which may be isomers of rubber.<sup>51</sup> Viscous and liquid polymers have also been obtained by carrying out the polymerization in the presence of boron trifluoride<sup>52</sup> and aluminum chloride.<sup>53</sup> Experiments have indicated that the dimer of butadiene, obtained by heating that hydrocarbon under pressure, is vinylcyclohexene.<sup>54</sup>

When isoprene is heated to 80°-90°C. for several days, or in sealed tubes at 150°C. for 6 to 7 days, liquid polymers as well as resinous substances are formed. At least two dimers are present in this mixture: namely, dipentene and  $\beta$ -myrcene or diprene, the formulas of which are:<sup>55</sup>



According to Whitby and Crozier,<sup>56</sup> the polymerization of pure isoprene and

<sup>50</sup> E. Eigenberger, *J. prakt. Chem.*, 1931, 129, 312; *Chem. Abs.*, 1931, 25, 2969. Cf. H. Staudinger, *British P.* 361,341, 1930, *Chem. Abs.*, 1933, 27, 998.

<sup>51</sup> G. S. Whitby and R. N. Crozier, *Can. J. Research*, 1932, 6, 203; *Brit. Chem. Abs. A.*, 1932, 861.

<sup>52</sup> F. Hofmann and M. Otto, *German P.* 505,265, 1926 and 512,959, 1927; *Chem. Abs.*, 1932, 26, 479. *British P.* 293,487, 1927; *Brit. Chem. Abs.*, B, 1928, 664.

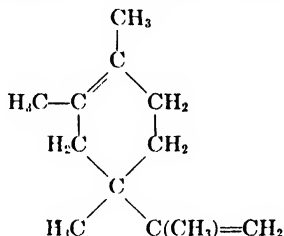
<sup>53</sup> H. Höber, *German P.* 557,805, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 304.

<sup>54</sup> F. Hofmann, *Z. angew. Chem.*, 1912, 25, 1465. *Chem. Abs.*, 1912, 6, 3025. *British P.* 343,116, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1931, 570. See also S. V. Lebedev, *J. Russ. Phys.-Chem. Soc.*, 1911, 43, 820, 1735; *Chem. Abs.*, 1912, 6, 478, 1373. S. V. Lebedev and N. A. Skavronskaya, *ibid.*, 1911, 43, 1124; 1913, 45, 1296; *Chem. Abs.*, 1915, 9, 798.

<sup>55</sup> I. I. Ostromislensky and F. F. Koschelev, *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 1928; *Chem. Abs.*, 1916, 10, 1947. O. Aschan, *Ann.*, 1924, 439, 221; *Chem. Abs.*, 1925, 19, 52; *Ber.*, 1924, 57, 1959; *Chem. Abs.*, 1925, 19, 647. T. Wagner-Jauregg, *Ann.*, 1931, 488, 176; *Chem. Abs.*, 1931, 25, 5139. For a more complete discussion of these dimers, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, 616.

<sup>56</sup> G. S. Whitby and R. N. Crozier, *Can. J. Research*, 1932, 6, 203; *Chem. Abs.*, 1932, 26, 2891.

dimethylbutadiene at temperatures of 10-145°C. does not afford, in either case, any dimer which is polymerizable to caoutchouc. The products isolated by these investigators were only cyclic dimers and are not regarded as intermediates in the formation of rubber-like substances. In the polymerization of 2,3-dimethylbutadiene<sup>67</sup> under similar conditions, much less oily materials and a higher proportion of rubbery polymers were formed than in the case of isoprene. The ratio of oil to rubber from a given diene is approximately constant in different periods of polymerization at a given temperature. Lebedev and Mereshkovski<sup>68</sup> consider that the dimer of 2,3-dimethylbutadiene possesses the constitution:



In the case of chloroprene, the formation of the volatile, oily  $\beta$ -polychloroprene<sup>69</sup> is favored by polymerization at elevated temperatures, e.g., at 60°C., in the absence of air and in the presence of antioxidants, which suppress the production of rubber-like polymers.  $\beta$ -Polychloroprene probably consists of cyclic dimers and other simple polymers. (See Chapter 8.)

**Rubber-like Polymers.** The formation of rubber-like or balata-like polymers from butadiene, isoprene, or 2,3-dimethylbutadiene proceeds slowly when these substances are warmed, or when they are allowed to stand at ordinary temperature in contact with catalysts.<sup>69</sup> Chloroprene, however, polymerizes spontaneously at ordinary temperatures and with a much greater speed. As previously stated, several qualitatively different types of material are produced depending upon the conditions. The first step of the process is probably the formation of long polymeric chains, consisting of units of the diolefin united by 1,4- addition. A consideration of the kinetics and general characteristics of these reactions suggests that the formation of rubbery or similar high-molecular-weight polymers from diolefins is the result of a chain reaction. This postulate is based on evidence indicating that such reactions are usually unimolecular,<sup>71</sup> are catalyzed by a wide variety of substances capable of acting as "trigger" molecules<sup>72</sup> and that they are inhibited by antioxidants as well as certain other substances. It follows, then, that the reaction is initiated by an activated diolefin molecule or by some other molecule acting as a "trigger."<sup>73</sup> Under conditions which inhibit the propagation

<sup>67</sup> For the production of oily polymers from 2,3-dimethylbutadiene, see P. Van Romburgh and G. Van Romburgh, *Proc. Roy. Acad. Amsterdam*, 1931, **34**, 224; *Chem. Abs.*, 1931, 25, 3309.

<sup>68</sup> S. V. Lebedev and B. K. Mereshkovski, *J. Russ. Phys.-Chem. Soc.*, 1913, **45**, 1249; *Chem. Abs.*, 1914, **8**, 320. See also I. L. Kondakov, *J. prakt. Chem.*, 1901, **64**, 109; *J.C.S.*, 1901, **80** (1), 625.

<sup>69</sup> W. H. Carothers, I. Williams, A. M. Collins and J. E. Kirby, *J.A.C.S.*, 1931, **53**, 4211.

<sup>70</sup> It is reported that a rubber-like resin results when 1,6-dimethyl-1,3,5-hexatriene is exposed to air. See Union, *Compt. rend.*, 1933, **196**, 353; *Chem. Abs.*, 1933, 27, 1859.

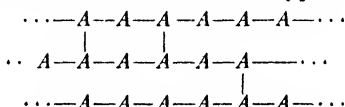
<sup>71</sup> J. B. Conant and C. O. Tongberg, *J.A.C.S.*, 1930, **52**, 1659. G. Tammann and A. Pape, *Z. anorg. allgem. Chem.*, 1931, **200**, 113; *Chem. Abs.*, 1932, 26, 23. J. A. Christiansen and H. A. Kramers, *Z. physik. Chem.*, 1923, **104**, 457; *J.C.S.*, 1924, **126** (2), 28.

<sup>72</sup> J. A. Christiansen and H. A. Kramers (*loc. cit.*) have proposed the theory that chain reactions are initiated by the action of an activated molecule of high energy content, the so-called "trigger" molecule. The activated molecule is believed to react either unimolecularly or with another molecule in such a way that the products must have the initial energy of activation plus the additional energy of reaction if it is exothermic. According to this mechanism it is possible for the "trigger" molecules to activate other molecules by transferring this energy through subsequent collisions. See also H. W. Starkweather and G. B. Taylor, *J.A.C.S.*, 1930, **52**, 4708.

<sup>73</sup> W. Chalmers, *Can. J. Research*, 1932, **7**, 113; *Chem. Abs.*, 1932, 26, 5480. W. H. Carothers, et al., *J.A.C.S.*, 1931, **53**, 4216.

of a chain mechanism, rubbery polymers are either not formed, or their formation is suppressed, and only lower polymers are produced. It appears, therefore, that as a result of the chain reaction, high-molecular-weight polymers somewhat resembling natural rubber are obtained. In natural rubber the isoprene units seem to be arranged in a very symmetrical manner, i.e., they are united regularly in 1,4-1,4 . . . order. However, in synthetic rubber there is good reason<sup>64</sup> to believe that a more or less irregular arrangement of isoprene-molecule units takes place; that is, arrangements such as 1,4-4,1 . . . and 4,1-1,4 . . . occur. In order to duplicate the properties of natural rubber, the isoprene would need to be polymerized under conditions leading to a regular arrangement of units in the polymer molecule. In view of the great complexity of the reaction, it is obvious that such a condition is enormously difficult of fulfillment and would necessitate a very special combination of circumstances. However,  $\mu$ -polychloroprene yields a sharp x-ray diffraction pattern, like natural rubber, but the same property is absent<sup>66</sup> from other synthetic rubbers. This indicates that a more regular arrangement of chloroprene units is present in the polychloroprene molecule, possibly owing to the orientating influence of the halogen atom. Irrespective of the manner in which the units are combined in synthetic rubber, the molecular weight and chain length approach very closely those of plasticized natural rubber.<sup>66</sup>

In other respects, moreover, the synthetic rubber-like substances from isoprene may display irregularities not exhibited by natural rubber. The molecules may be coiled into spirals rather than rigidly extended. Also, there is a possibility of geometrical isomerism so that irregular arrangements such as *cis-cis-cis*— or *trans-trans-trans*— . . . may exist. Finally, there is a possibility of cross-linking of chains at occasional points to produce a structure of the type:



Since each isoprene (or diolefin) unit in the polymeric complex still has one unsaturated linkage, cross-linking of several polymeric macromolecules can take place until finally all these points of unsaturation are fully saturated and a complex polycyclic material will be formed. It seems highly probable that such "cyclorubbers" are actually formed during the polymerization of diolefins in the presence of various catalysts. For instance, the granular, cauliflower-like varieties of synthetic rubbers which are obtained by very slow polymerization, and also in the presence of sodium, are probably formed by a cross-linking of polymer chains, i.e., they are likely to be cyclic in structure. Such materials<sup>67</sup> are tough, nonplastic, difficult to mill, and show little resemblance to natural rubber.

**Conditions for the Conversion of Diolefins into Rubber-like Polymers.** The earlier workers on the polymerization of isoprene employed hydrochloric acid and nitrosyl chloride as condensing agents. Later, isoprene was found to be rapidly converted into rubber-like substances under the influence of ordinary light,<sup>68</sup> ultraviolet light,<sup>69</sup> and the silent electric discharge,<sup>70</sup> and it has

<sup>64</sup> T. Midgley and A. L. Henne, *J. A. C. S.*, 1930, 52, 2077. See also T. Midgley, A. L. Henne and A. F. Shepard, *J. A. C. S.*, 1932, 54, 381.

<sup>65</sup> See G. L. Clark, *Ind. Eng. Chem.*, 1929, 21, 128.

<sup>66</sup> A. J. Wildschut, *Rec. trav. chim.*, 1933, 52, 935; *Rubber Chem. Tech.*, 1934, 7, 34; *Chem. Abs.*, 1934, 28, 927, 4028.

<sup>67</sup> For example the  $\beta$ -polychloroprenes described by W. H. Carothers, I. Williams, A. M. Collins, and J. E. Kirby, *J. A. C. S.*, 1931, 53, 4211. Also the methyl rubber H, prepared from dimethylbutadiene. See E. Weil, *Ind. Eng. Chem.*, 1926, 18, 1174.

<sup>68</sup> O. Wallach, *Ann.*, 1887, 239, 48; *J. C. S.*, 1887, 52, 905. S. V. Lebedev, *J. Russ. Phys.-Chem. Soc.*, 1909, 41, 1868; 1910, 42, 949; *J. C. S.*, 1911, 100 (1), 26. See also G. Scagliarini and G. Saladini, *Gazz. chim. ital.*, 1923, 53 (1), 135; *J. C. S.*, 1923, 124 (1), 587.

<sup>69</sup> C. Harries, *Ann.*, 1913, 395, 266; *Chem. Abs.*, 1913, 7, 1983. I. Ostromislensky, *J. Russ. Phys.-*

been stated that these influences are superior to all chemical catalysts with the exception of oxygen or certain oxygenated substances. In 1910, Harries noted that isoprene could be polymerized to rubber by heating it with glacial acetic acid in a sealed tube at 100°C. The product could be vulcanized and was evidently superior to any previously prepared. About the same time, Matthews and Strange<sup>71</sup> found that metallic sodium was a catalyst for the conversion of isoprene into rubber. The use of sodium in an atmosphere of carbon dioxide was also developed by the Badische Co. Nevertheless, though isoprene is converted at 60°C. in from 50 to 100 hours almost quantitatively into caoutchouc, this material possesses properties different from those of synthetic products prepared in other ways;<sup>72</sup> that is, the sodium-polymerized product is probably differently cyclized by cross-linking of several polymer-chains.

Hofmann<sup>73</sup> and his collaborators reported that pure isoprene could be polymerized by mere heat treatment to give a material capable of being cured. This was probably the first time that a synthetic product was developed corresponding in any degree with the technical requirements of rubber. The heat-treatment process was utilized successfully for the manufacture of rubber from 2,3-dimethylbutadiene during the World War.

Harries<sup>74</sup> outlined three methods of polymerizing butadiene and its simple homologues: (1) heat treatment, by itself or in conjunction with glacial acetic acid, for several months at 60-100°C., (2) heating, or allowing the hydrocarbon to stand in the presence of metallic sodium in an atmosphere of carbon dioxide, and (3) heating with peroxides, especially benzoyl peroxide. Since that time a large number of catalysts have been developed for accelerating or controlling the polymerization of diolefins. Also, the method of polymerizing diolefins in aqueous emulsion has been developed. Even before the War the chemists of the Bayer Co. had learned that both the yield and the properties of isoprene rubber were improved by carrying out the polymerization in a sealed vessel in the presence of an aqueous preparation of a protein. The polymerization of emulsified diolefinic hydrocarbons presents one of the satisfactory methods for the synthesis of rubber-like materials on a technical scale.

#### CATALYSTS FOR THE SYNTHESIS OF RUBBER

Though the usual active polymerizing agents such as concentrated sulphuric acid, aluminum chloride,<sup>75</sup> stannic chloride, antimony halides,<sup>76</sup> boron trifluoride,<sup>77</sup> and titanium tetrachloride,<sup>78</sup> are known to convert isoprene and similar 1,3-diolefins

*Chem. Soc.*, 1912, 44, 204; *J.C.S.*, 1912, 102 (1), 280. R. Pummerer and H. Kehlen, *Ber.*, 1933, 66, 1107; *Chem. Abs.*, 1933, 27, 6018. German P. 576,141, 1933; *Chem. Abs.*, 1933, 27, 3721. R. Pummerer and H. Kehlen, *Rubber Chem. Tech.*, 1934, 7, 184; *Chem. Abs.*, 1934, 28, 4628.

<sup>70</sup> J. Collie, *J.C.S.*, 1905, 87, 1540.

<sup>71</sup> F. E. Matthews and E. H. Strange, *British P.* 24,790, 1910; *J.S.C.I.*, 1911, 30, 1398. French P. 437,547, 1910; *J.S.C.I.*, 1912, 31, 503.

<sup>72</sup> C. Harries, *Ann.*, 1911, 383, 157; *Chem. Abs.*, 1911, 5, 3519.

<sup>73</sup> F. Hofmann and C. Coutelle, *Canadian P.* 143,493, 1912; *Chem. Abs.*, 1913, 7, 427. F. Hofmann, C. Coutelle, K. Meisenburg and K. Delbruck, *Canadian P.* 143,489, 1912; *Chem. Abs.*, 1913, 7, 426. *Cf.* U. S. P. 1,062,828, 1,062,912, 1,062,913, 1,062,914, May 27, 1913; *Chem. Abs.*, 1913, 7, 2485. F. Hofmann and C. Coutelle, U. S. P. 1,069,951, 1,070,258, 1,070,259, Aug. 12, 1913; *Chem. Abs.*, 1913, 7, 3424. See also R. Weil, *Ind. Eng. Chem.*, 1926, 18, 1174.

<sup>74</sup> C. D. Harries, "Untersuchungen über die natürlichen und künstlichen Kautschukarten," Julius Springer, Berlin, 1919, 170.

<sup>75</sup> *British P.* 358,068, 1931, to N. V. Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs.*, B, 1932, 172. N. D. Zelinsky, Y. I. Denisenko, M. S. Evantova and S. I. Khromov, *Sintet. Kauchuk*, 1933, 4, 11; *Chem. Abs.*, 1934, 28, 3617.

<sup>76</sup> H. von Euler and L. Ahlström, *Arkiv Kemi, Mineral Geol.*, 1932, 11A (2), 1; *Chem. Abs.*, 1933, 27, 950. See also H. von Euler and H. Willstaedt, *ibid.*, 1929, 10B, (9), 1; *Chem. Abs.*, 1929, 23, 4465.

<sup>77</sup> F. Hofmann, M. Otto and W. Stegman, U. S. P. 1,885,060, Oct. 25, 1932; *Chem. Abs.*, 1933, 27, 1006. German P. 504,730, 1933, and 507,919, 1933; *Chem. Abs.*, 1933, 27, 4816. German P. 204,925, 1912, to F. Bayer & Co.; *J.S.C.I.*, 1913, 32, 1078.

<sup>78</sup> T. Wagner-Jauregg, *Ann.*, 1932, 496, 52; *Brit. Chem. Abs.*, A, 1932, 866.

into polymers, the products are stated to be of little value as rubber substitutes. A possible explanation of this fact is that cross-linking of the polymeric chains proceeds very rapidly and a complex polycyclic structure is produced with properties unlike those of ordinary rubber.<sup>70</sup> Aryl diazonium fluoborates<sup>80</sup> are said to be quite effective in catalyzing the polymerization of indene, styrene, cyclopentadiene, phenyl butadiene, pinene, isoprene and other similar compounds. The catalytic influence of peroxides, per-acids, oxidized substances and oxygen itself on the polymerization of all types of unsaturated substances including styrene and isoprene has been recognized for many years.<sup>81</sup> Organic peroxides, metal oxides, per-salts,<sup>82</sup> and the products obtained by ozonizing isoprene<sup>83</sup> have all been proposed as catalysts for the conversion of isoprene into rubber.<sup>84</sup> Conant and Tongberg<sup>85</sup> have shown that a partially ozonized sample of isoprene polymerized more rapidly under high pressure than did unozonized isoprene. The polymerization of 2,3-dimethylbutadiene is accelerated at room temperature by the presence of 4 per cent or less of ozonized diisobutylenes.<sup>86</sup> From experiments on isoprene and dimethylbutadiene in the presence of oxygen, Staudinger and Lautenschläger<sup>87</sup> conclude that polymerization is accelerated by autoxidation and that the active polymerizing catalyst is probably a primary peroxide (not isolated) rather than the isolated polymerized peroxides. In the polymerization of styrene, however, oxygen is less active than benzoyl peroxide and diisobutylene ozonide is even more active as a catalyst than the latter.<sup>88</sup>

The application of metallic sodium as a catalyst for the polymerization of 1,3-dienes has already been described. However, according to Zelmanov and Shalnikov<sup>89</sup> the adoption of colloidal sodium is a decided improvement over the old method. Solid polymers from butadiene were obtained in 2-36 hours at 10-15°C. using only 0.001 to 0.3 per cent of sodium as the catalyst. The catalyst was prepared by condensing sodium and butadiene on a cooled surface, simultaneously. Various derivatives of the alkali metals, including sodium amide or alkali metal alkyls,<sup>90</sup> have been used for this purpose. Diazoaminobenzene is said to catalyze the polymerization of butadiene obtained from petroleum fractions.<sup>91</sup> A number of other apparently unrelated materials have been suggested, including glycerol, starch and urea.<sup>92</sup>

#### COMMERCIAL ATTEMPTS TO SYNTHESIZE RUBBER

Attempts have been made to develop the synthesis of rubber on a commercial scale, especially in Germany, but so far without success. The low price of natural

<sup>70</sup> The production of resins from nuxtures of diolefins and olefins under the influence of anhydrous aluminum chloride is considered later.

<sup>80</sup> H. A. Bruson, U. S. P. 1,892,101, Dec. 27, 1932, to Resinous Products & Chemical Co.; *Chem. Abs.*, 1933, 27, 1893.

<sup>81</sup> C. Engler, 8th Int. Congr. Appl. Chem., 1912, 25, 661; *Chem. Abs.*, 1913, 7, 2301.

<sup>82</sup> F. Klatte and A. Rollet, U. S. P. 1,241,733, Oct. 2, 1917, to Chem. Fabr. Griesheim-Elektron; *Chem. Abs.*, 1918, 12, 231. German P. 281,688, 1914; *J.S.C.I.*, 1915, 34, 623.

<sup>83</sup> H. S. A. Holt and G. Steimig, U. S. P. 1,189,110, June 27, 1916; *Chem. Abs.*, 1916, 10, 2162. British P. 22,454, 1911, to Badische Anilin- & Soda-Fabrik; *J.S.C.I.*, 1912, 31, 1085.

<sup>84</sup> Exposure to a concentrated electromagnetic field having waves of length 3 mm. to 6 m. is said to accelerate the polymerization of isoprene. See British P. 417,501, 1934, to Ternion A.-G.; *Chem. Abs.*, 1935, 29, 1178.

<sup>85</sup> J. B. Conant and C. O. Tongberg, *J.A.C.S.*, 1930, 52, 1659.

<sup>86</sup> R. C. Houts and H. Adkins, *J.A.C.S.*, 1931, 53, 1058.

<sup>87</sup> H. Staudinger and L. Lautenschläger, *Ann.*, 1931, 488, 1; *Chem. Abs.*, 1931, 25, 5138.

<sup>88</sup> R. C. Houts and H. Adkins, *J.A.C.S.*, 1933, 55, 1609.

<sup>89</sup> I. L. Zelmanov and A. I. Shalnikov, *J. Phys. Chem.*, (U. S. S. R.), 1933, 4, 353; *Chem. Abs.*, 1933, 27, 6016. See also S. A. Vekshinsky, Russian P. 32,723, 1933; *Chem. Abs.*, 1934, 28, 3618.

<sup>90</sup> German P. 255,786, 1912, to Badische Anilin- & Soda-Fabrik; *Chem. Abs.*, 1913, 7, 1815. See also K. Ziegler, F. Crösemann, H. Kleiner and O. Schäfer, *Ann.*, 1929, 473, 1, 57, *Chem. Abs.*, 1921, 23, 5181.

<sup>91</sup> M. A. Lure and V. A. Ignatyuk, *Sintet Kauchuk*, 1932 (3), 12; *Chem. Abs.*, 1933, 27, 6016. B. V. Bysov, *J. Appl. Chem. Russia*, 1933, 6, 1074; *Brit. Chem. Abs. B.*, 1934, 245.

<sup>92</sup> German P. 248,390, 1911, to F. Bayer & Co.; *Chem. Abs.*, 1912, 6, 2856.



rubber at the present time would appear to render impossible a successful rubber synthesis unless the synthetic product possessed special properties and was particularly adaptable for certain purposes. Before the World War, attempts to convert isoprene into a technical rubber product were made by the Bayer Co. and others, but, although several commercially practicable syntheses of isoprene from acetylene, or amyl alcohols, were developed, no real technical advance resulted. During the War, a process was developed in Germany by the Bayer Co. whereby about 150 tons of dimethylbutadiene rubber (methyl rubber) were made per month with a total production of 2350 tons.<sup>93</sup> The 2,3-dimethylbutadiene was synthesized from acetylene via acetone and pinacol. A small amount of a somewhat unstable methyl rubber was later prepared from 2,3-dimethylbutadiene by the Badische Co. using the sodium-carbon dioxide method. However, most of the methyl rubber was prepared by heat treatment and two types of product were obtained; namely, methyl rubber W and methyl rubber H.

FIG. 47.

Methyl Rubber, a Product Obtained by the Polymerization of Dimethylbutadiene.

Courtesy G. S. Whitby



**Methyl Rubber W.** Crude methyl rubber W<sup>94</sup> was produced by keeping liquid 2,3-dimethylbutadiene in large double-walled vessels for about five months at 70°C. The entire contents of the vessel were thereby converted into a tough, rubber-like, greenish yellow, translucent mass. This material was difficult to work on the mill and required large amounts of organic or inorganic fillers. Its use in soft-rubber goods was suggested.

**Methyl Rubber H.** The so-called "methyl rubber H" was made by filling thin-walled tin-plate vessels about one-third full of dimethylbutadiene and storing them for about two months at 30°C. To hasten the process the batch was inoculated with previously polymerized material.<sup>95</sup> The product was a white, porous, cauliflower-like mass with little resemblance to raw rubber. (See Fig. 47.) On a hot mill the substance first crumbled but soon milled to a smooth sheet, still retaining a certain dryness and granular consistency.

According to Weil,<sup>96</sup> these synthetic products possessed decided disadvantages when compared with natural rubber. For example, they did not show a true

<sup>93</sup> It. Weil, *Ind. Eng. Chem.*, 1926, 18, 1174.

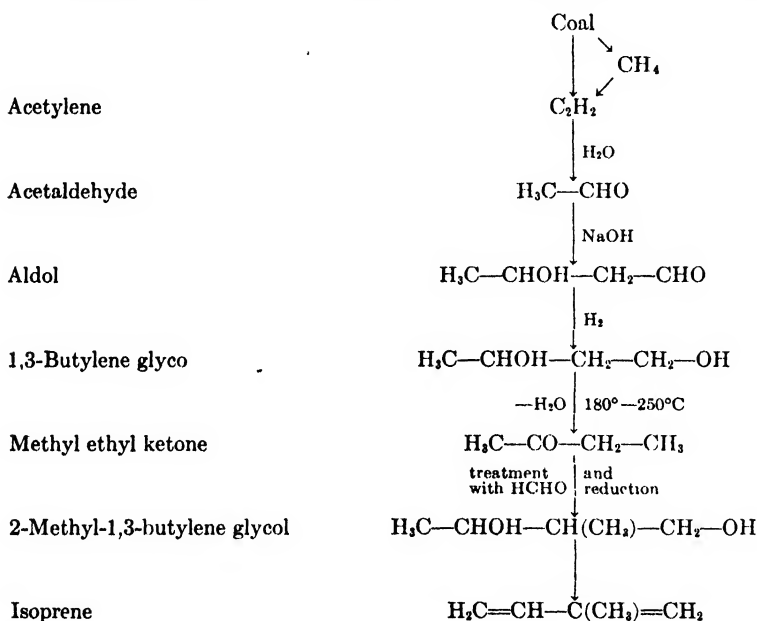
<sup>94</sup> The history of dimethylbutadiene synthetic rubber research has been reviewed by V. A. Getling and N. V. Zhdanova, *Sintet. Kauchuk*, 1933, 5, 15; *Chem. Abs.*, 1934, 28, 3615.

<sup>95</sup> Methyl rubber H in properties and autocatalytic mode of formation appears to be closely analogous to the  $\omega$ -polychloroprene described by W. H. Carothers, I. Williams, A. M. Collins and J. E. Kirby, *J.A.C.S.*, 1931, 53, 4214. See Chapter 8.

<sup>96</sup> R. Weil, *loc. cit.*

plasticity, lacked elasticity, were deficient in adhesive strength, and showed instability, although the latter defect could be overcome by the addition of preservatives such as 1,8-diaminonaphthalene. Methyl rubber, particularly the H variety, found successful application in electrical insulation, especially in the cable industry, in the manufacture of steam- and air-brake hose for railways, and for insulation in batteries. For use in tire manufacture, these synthetic products were not very satisfactory, being lacking in elasticity.<sup>97</sup>

More recent developments in the problem of synthesizing rubber include the work of the I. G. Farbenindustrie A.-G. in Germany, and E. I. du Pont de Nemours & Co. in the United States. It has also been reported that a synthetic-rubber industry is being organized in Russia.<sup>98</sup> In the production of artificial rubber as undertaken by the I. G. Farbenindustrie A.-G., isoprene<sup>99</sup> constitutes the raw material. The synthesis of the latter is indicated in the following series of reactions:



The resulting isoprene is polymerized to rubber by heating it with water, or caustic alkali, at 100°C. in the presence of acids, alkali metals, oxidizing agents, emulsifiers and a buffer system of  $\text{pH}$  4.8-5.0.

A product bearing the name of Polynit is prepared from butadiene by sodium polymerization or, better, by warming an emulsion of that hydrocarbon with ammonium oleate. The polymerized product is baked at 150°C. for two hours giving an infusible material insoluble in all solvents and chemically quite resistant.<sup>100</sup>

<sup>97</sup> For the vulcanization of methyl rubber, see G. S. Whitby and M. Katz, *Can. J. Research*, 1932, 6, 398; *Chem. Abs.*, 1932, 26, 4204.

<sup>98</sup> See *J.S.C.I.*, 1932, 51, 604. Also S. V. Lebedev, *Sotsialist Rekonstruktsiya i Nauka*, 1932, 3 (1), 127; *Chimie et industrie*, 1934, 32, 1150; *Chem. Abs.*, 1935, 29, 2390.

<sup>99</sup> G. Kessel, *Chem.-Tech. Rundschau*, 1930, 45, 135; *Chem. Abs.*, 1930, 24, 3922. See British P. 320,362, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1930, 305.

<sup>100</sup> Butadiene may be prepared by the dehydration of 1,3-butylene glycol in the presence of alum or a mixture of calcium and sodium phosphates at 240-250°C. The glycol is synthesized from acetylene via acetaldehyde and aldol. See British P. 291,748, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1929, 886. French P. 659,314, 1928; *Chem. Abs.*, 1929, 23, 5197.

The synthesis of rubber and a vulcanized rubber-like substance ( $\alpha$ - and  $\mu$ -polychloroprenes) from 2-chlorobutadiene has been described in Chapter 8.

A complete survey of the vast literature of synthetic rubber production might easily occupy several volumes.<sup>101</sup> In the following abbreviated account, the main trend of investigation is summarized as concisely as possible. Three main methods of polymerizing butadiene and its simple homologues, particularly isoprene and 2,3-dimethylbutadiene, have been developed: (1) heat-polymerization usually in the presence of an oxygen or other catalyst; (2) alkali-metal polymerization; and (3) polymerization in the form of an emulsion and usually in the presence of catalysts. The latter method yields a synthetic latex capable of being precipitated to form a rubbery mass.

In connection with the polymerization of diolefins to substances resembling rubber, certain mechanical details relating to temperature control, handling of the reactants or products and type of apparatus employed, seem to be worthy of brief mention inasmuch as they contribute a great deal to the success of the operation. An effective device for avoiding the deleterious action of excess heat upon unreacted diolefins<sup>102</sup> consists of a vessel called a "moderator." The vessel contains no polymerizing agent. The device is connected to the reaction vessel in such a way that the excess heat liberated during the reaction causes the diolefin to distil over into the "moderator." When the reaction has subsided, the diolefin is returned to the reaction vessel. To facilitate the removal of the polymerization products from the vessel, various coatings and linings have been suggested.<sup>103</sup> Readily removable materials such as paper, cardboard, textile fabrics and leather are advocated. These materials may be coated with a nitrocellulose or gelatin varnish. Waxes, bitumens, water glass and polymers of diolefins are also said to be of assistance in removing the reaction-mass. Double-walled vessels for "sodium" polymerizations have been described<sup>104</sup> in which the hydrocarbons may come in contact with the sodium through connecting holes of at least 2 mm. diameter. Polymerization in the presence of alkali or alkaline earth metals is favored by metal vessels having smooth, highly polished inner surfaces free from edges.<sup>105</sup>

**The "Emulsion" Method.** In this process, which is probably the most important of the three methods outlined above, the conjugated diolefin is emulsified with water and the resulting emulsion allowed to polymerize by maintaining at about 50-70°C. for several days. The proportion of water used in the emulsion need not be very great,<sup>106</sup> since successful polymerizations have resulted when the amount of water was insufficient to completely dissolve the emulsifying agents. A large variety of emulsifying agents have been suggested, but sodium oleate, sodium isobutyl-naphthalene sulphonate and egg albumin are most frequently employed.<sup>107</sup> The emulsion is maintained at a pH of 4.0-8.5 by buffering with sodium phosphate. The emulsion may be homogenized before polymerization.<sup>108</sup> Colloids

<sup>101</sup> For articles on the development of synthetic rubber, see F. Jacobs, *Rev. gen. caoutchouc*, 1932, 9 (81), 19; 9 (83), 9; *Chem. Abs.*, 1932, 26, 4731. W. C. Calvert, *India Rubber Rev.*, 1928, 9, 48; *Chem. Abs.*, 1929, 20, 3685. G. S. Whitby and M. Katz, *Ind. Eng. Chem.*, 1933, 25, 1204, 1338.

<sup>102</sup> French P. 687,721, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 758.

<sup>103</sup> C. Heuck and H. Enderlein, U. S. P. 1,809,445, June 9, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4282. British P. 336,389, 1929; *Chem. Abs.*, 1931, 25, 2022. French P. 689,824, 1930; *Chem. Abs.*, 1931, 25, 963.

<sup>104</sup> French P. 697,679, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3200.

<sup>105</sup> German P. 540,224, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1620.

<sup>106</sup> French P. 720,189, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3960.

<sup>107</sup> M. Luther and C. Heuck, U. S. P. 1,896,491, Feb. 7, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2843. U. S. P. 1,864,073, June 21, 1932; *Chem. Abs.*, 1932, 26, 4505. British P. 294,963, 1927; *Chem. Abs.*, 1929, 23, 2071. French P. 647,041, 1928; *Chem. Abs.*, 1929, 23, 2603. French P. 658,359, 1928; *Chem. Abs.*, 1929, 23, 5362. German P. 558,890, 1927; *Chem. Abs.*, 1933, 27, 632. See also R. P. Dinmore, British P. 297,050, 1927, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1929, 23, 2603. E. Techunkur and W. Bock, German P. 570,980, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4441.

<sup>108</sup> H. Lecher and A. Koch, U. S. P. 1,789,873, Jan. 30, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1412. German P. 526,304, 1928; *Chem. Abs.*, 1931, 25, 4443. British P. 304,923, 1928; *Chem.*

such as carrageen moss extract, gum arabic, and higher alcohols are used to facilitate emulsification.<sup>109</sup> Emulsions of butadiene hydrocarbons in water may be prepared also in the presence of the hydrochloride or acetate of certain high-molecular-weight bases, such as diethylaminoethyloleamide and 2-n-pentadecylglyoxalidine.<sup>110</sup> Polymerization is effected by maintaining the emulsion at 50-70°C. for several days.

Lecher and Koch<sup>111</sup> effectively polymerized a butadiene hydrocarbon by employing two emulsifying agents, one being soluble in water (sodium oleate) and the other soluble in the hydrocarbon (magnesium oleate). The reaction is completed after 5-6 days of heating at 60-70°C. However, the presence of oxygen or substances yielding oxygen has been found to speed up the process and to increase the yield. Perborates,<sup>112</sup> hydrogen peroxide,<sup>113</sup> benzoyl peroxide, manganese borate<sup>114</sup> and colloidal or finely divided metallic oxides such as manganese dioxide and lead dioxide, as well as the oxides of mercury, silver, nickel, cobalt and chromium have been used.<sup>115</sup> Emulsions of 1,3-dienes in water may be polymerized in the presence of hydrazine or its derivatives, e.g., hydrazoisobutyric acid, hydrazine dicarboxylic acid, ethyl ester or sodium phthalyl hydrazide.<sup>116</sup> Emulsified diolefins may, in addition, be polymerized in the presence of hexachloroethane, carbon tetrachloride, ethylene dichloride, chlorobenzene, sodium trichloroacetate, and similar chlorinated compounds.<sup>117</sup> Amyl ether<sup>118</sup> has also been used for this purpose. Benzene-soluble rubbery polymers are obtained by carrying out the polymerization in emulsion at 10-20°C. and arresting the polymerization when 20 to 30 per cent of the diolefin remains unpolymerized.<sup>119</sup> A rubber-like product<sup>120</sup> results when an aqueous emulsion of a vegetable oil, e.g., tung oil, is polymerized with butadiene or isoprene in the presence of oxygen or an oxidizing compound. Another emulsion-polymerization<sup>121</sup> carried out in the presence of oxidizing agents yields polymers free from difficulty soluble substances by including such additional compounds as phenols, hydroquinone, resorcinol, pyrocatechol, acetic acid and acetone. Iodine, colloidal sulphur and arsenious acid are also said to be useful for this purpose.

Where hydrogen peroxide or similar oxidizing agents are used to effect conversion, reducing materials, such as sodium bisulphite, sodium hydro-bisulphite, or

*Abs.*, 1930, 24, 266 French P. 670,996, 1929; *Chem. Abs.*, 1930, 24, 2008. See also British P. 307,938, 1928; *Chem. Abs.*, 1930, 24, 266

<sup>109</sup> British P. 320,560, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2640 British P. 313,188, 1928; *Chem. Abs.*, 1930, 24, 990.

<sup>110</sup> W. Bock and E. Tschunker, U. S. P. 1,924,227, Aug. 29, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5577. German P. 511,145, 1927; *Chem. Abs.*, 1931, 25, 1412. German P. 555,585, 1928; *Chem. Abs.*, 1932, 26, 6184. British P. 330,272, 1928; *Brit. Chem. Abs.* B, 1930, 873. French P. 681,896, 1929; *Chem. Abs.*, 1930, 24, 4425.

<sup>111</sup> H. Lecher and A. Koch, U. S. P. 1,851,104, Mar. 29, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3144. German P. 526,498, 1928; *Chem. Abs.*, 1931, 25, 4443.

<sup>112</sup> British P. 283,840, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 4274. French P. 647,041, 1928; *Chem. Abs.*, 1929, 23, 2603.

<sup>113</sup> A. T. Maximoff, U. S. P. 1,910,846 and 1,910,847, May 23, 1933, to Naugatuck Chem. Co.; *Brit. Chem. Abs.* B, 1934, 159. British P. 292,103, 1928; *Brit. Chem. Abs.* B, 1929, 864.

<sup>114</sup> E. Tschunker and W. Bock, U. S. P. 1,935,733, Nov. 21, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 932.

<sup>115</sup> H. Meis, W. Klein and E. Tschunker, U. S. P. 1,896,493, Feb. 7, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2845. German P. 515,143, 1927; *Chem. Abs.*, 1931, 25, 1706. British P. 317,030, 1928; *Brit. Chem. Abs.* B, 1929, 829. French P. 656,428, 1929; *Chem. Abs.*, 1929, 23, 4103. See also British P. 294,661, 1927; *Chem. Abs.*, 1929, 23, 2071.

<sup>116</sup> O. Schmidt and B. von Bock, German P. 504,436, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 6308. British P. 333,894, 1929; *Chem. Abs.*, 1931, 25, 845.

<sup>117</sup> W. Bock and E. Tschunker, U. S. P. 1,898,522, Feb. 21, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2845. British P. 349,499, 1930; *Chem. Abs.*, 1932, 26, 5452. German P. 532,271, 1930; *Chem. Abs.*, 1932, 26, 337.

<sup>118</sup> British P. 306,350 and 306,944, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 438.

<sup>119</sup> C. Heuck, German P. 596,769, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5285. British P. 364,089, 1930; *Chem. Abs.*, 1933, 27, 1784. French P. 708,807 and 708,808, 1931; *Chem. Abs.*, 1932, 26, 1475.

<sup>120</sup> British P. 362,845, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 223. O. Ambrose and H. Reindel, German P. 526,305, 1928; *Chem. Abs.*, 1931, 25, 4443.

<sup>121</sup> French P. 686,934, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 845.

stannous chloride, are added to the polymerized latex to decompose excess oxidizing agent and to give paler products.<sup>122</sup> Emulsion polymerization is said to be facilitated by the presence of an unsaturated nitrile of acrylic acid or its methyl or butyl esters.<sup>123</sup> Polymerization of olefins of the butadiene type<sup>124</sup> has been effected, moreover, in the presence of compounds such as ethyl sorbate, ethyl cinnamate, 2-methyl-3-chlorobutadiene, 3-chlorostyrene and sorbic acid methyl ketone,  $\text{HOOC}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_2-\text{CO}-\text{CH}_3$ . By aqueous extraction of the cortex of rubber trees a non-rubber substance is obtained which is recommended as a catalyst for the emulsion-polymerization of diene hydrocarbons.<sup>125</sup> Rubber-like products of high elasticity and strength are obtained upon vulcanization in the presence of finely divided carbon.<sup>126</sup> A creamy or jelly-like product results<sup>127</sup> when butadiene hydrocarbons are stirred or shaken with aqueous solutions of the polymerization promoters.

The coagulation of the emulsified polymerization products may be accomplished by several methods. A common procedure consists in cooling the batch below 0°C.<sup>128</sup> The addition of salts of the alkali metals,<sup>129</sup> e.g., sodium chloride, sodium carbonate and sodium hydrogen phosphate is also quite effective. Such emulsions may be concentrated by standard methods in the presence of sodium oleate or other protective colloids.<sup>130</sup> The use of proteolytic enzymes<sup>131</sup> including papain, pancreas extract or banana juice has been recommended for this purpose. In every instance, the removal of unchanged diolefin before coagulation is advantageous.<sup>132</sup>

**"Sodium" Polymerization.** This polymerization is effected by agitating a mixture of the diolefin and an alkali metal or an alloy.<sup>133</sup> The polymerization may be carried out in successive stages by varying the temperature of reaction. For example, butadiene is treated with sodium amalgam at 0-6°C. for two days. The temperature is then raised to 30-40°C., sodium is added and the mixture allowed to stand for several days.<sup>134</sup> A catalyst of sodium particles of uniform size (balls of 1.1 mm. diameter) obtained by comminuting in a liquid and sieving, is said to be effective.<sup>135</sup> A convenient catalyst for polymerizing butadiene at 35-45°C. consists of sodium dispersed in a finely divided solid diluent, i.e., 1.5 parts of sodium ground

<sup>122</sup> M. Luther and C. Heuck, U. S. P. 1,860,681, May 31, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3804. German P. 543,152, 1928; *Chem. Abs.*, 1932, 26, 2621. British P. 323,721, 1928; *Brit. Chem. Abs. B.*, 1930, 251.

<sup>123</sup> E. Konrad and E. Tschunkur, U. S. P. 1,973,000, Sept. 11, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 7072. British P. 360,821 and 360,822, 1930; *Chem. Abs.*, 1933, 27, 1236. French P. 715,982 and 715,983, 1931; *Chem. Abs.*, 1932, 26, 2085.

<sup>124</sup> British P. 387,381, 1933, addn. to 339,355 and 342,314, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4718.

<sup>125</sup> W. A. Gibbons and E. M. McColm, U. S. P. 1,953,169, Apr. 3, 1934, to Naugatuck Chemical Co.; *Chem. Abs.*, 1934, 28, 3940.

<sup>126</sup> E. Tschunkur and W. Bock, German P. 532,456, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 337.

<sup>127</sup> A. Beck and M. Luther, German P. 533,885, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 876.

<sup>128</sup> E. Konrad and W. Siefken, U. S. P. 1,874,546, Aug. 30, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 6182. German P. 537,032, 1928; *Chem. Abs.*, 1932, 26, 1157. British P. 304,207, 1928; *Chem. Abs.*, 1929, 23, 4848. French P. 667,256, 1929; *Chem. Abs.*, 1930, 24, 1250.

<sup>129</sup> F. Schwerdtel, U. S. P. 1,879,548, Sept. 27, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 441. German P. 555,556, 1929; *Chem. Abs.*, 1932, 26, 1475. British P. 346,785, 1930; *Chem. Abs.*, 1932, 26, 2084.

<sup>130</sup> British P. 313,440, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1931, 78.

<sup>131</sup> British P. 307,375, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1929, 367.

<sup>132</sup> British P. 311,381, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 990.

<sup>133</sup> For a study of the mechanism involved in alkali-metal polymerization of diolefins see K. Ziegler, F. Dersch and H. Wollthian, *Ann.*, 1934, 511, 13. K. Ziegler and L. Jakob, *ibid.*, 45. K. Ziegler, L. Jakob, H. Wollthian and A. Wenz, *ibid.*, 64; *Chem. Abs.*, 1934, 28, 5430.

<sup>134</sup> M. Luther and C. Heuck, German P. 533,886, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 876.

<sup>135</sup> G. Ebert, F. A. Fries, and P. Garbsch, U. S. P. 1,880,918, Oct. 4, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 514. British P. 338,534, 1929; *Brit. Chem. Abs. B.*, 1931, 237. French P. 696,149, 1930; *Chem. Abs.*, 1931, 25, 2878.

with 60 parts of dry sodium chloride.<sup>136</sup> Besides metallic sodium, various alloys and derivatives of that element have been particularly recommended as catalysts. Midgley, Hochwalt and Thomas<sup>137</sup> use an alloy of sodium and potassium which is liquid under the conditions of reaction, for polymerizing diolefins. Polymerization can be effected in the presence of sodium, potassium, calcium and their alloys or organic compounds of alkali or alkaline earth metals which are not capable of ionization, such as sodium ethyl, sodium triphenylmethyl and lithium alkyls. The catalyst is added in three or more fractions.<sup>138</sup> The polymerization is carried out in an atmosphere of nitrogen, carbon dioxide or other inert gas. Diluents which may facilitate the reaction include dioxane, vinyl ether, vinyl chloride and acetals. The use of hydrogen is said to be advantageous; increase in hydrogen pressure lowers the viscosity of the polymerized product.<sup>139</sup> Butadiene hydrocarbons may also be polymerized in the presence of sodium hydride<sup>140</sup> or of sodium with addition of small quantities of water during reaction.<sup>141</sup> The water is added in the form of water of crystallization of salts (e.g.,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$  or  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ).

The polymerization reaction employing metallic sodium, or alkali metals generally, is accelerated or modified considerably by various organic materials. Thus the presence of hydrocarbon diluents such as butylene, cyclohexane, benzene, turpentine or gasoline is said to be advantageous. The greater the amount of diluent used, the greater is the proportion of polymerization product soluble in benzene and the lower is the viscosity of the solutions obtained.<sup>142</sup> Readily soluble rubber-like products are obtained by polymerizing in the presence of sodium, using solvents or dispersion media such as decahydronaphthalene, dry xylene, toluene, tetrahydronaphthalene, benzene, cyclohexane or liquid polymerization products of the process.<sup>143</sup> For example, Schmidt<sup>144</sup> prepared a thinly viscous product by polymerizing butadiene with sodium in the presence of cyclohexane. The material was recommended as a protective coating for wood and metal. Soluble plastic polymerization products are also obtained by continuously removing the soluble substances as formed, employing light petroleum, ether or benzene as solvent.<sup>145</sup>

Among the numerous substances which have been said to exercise a favorable influence on the polymerization of diolefins to rubber-like substances, in the presence of sodium or an alkali metal, the following may be mentioned:

- (1) Starch, cellulose, or cellulose ether.<sup>146</sup>
- (2) Ethyl or phenyl ether or an olefin oxide or peroxide.<sup>147</sup>
- (3) Ammonia or a free cyclic or aliphatic base to the extent of 0.01 to 1 per cent of the hydrocarbon polymerized.<sup>148</sup>

<sup>136</sup> L. van Zutphen, U. S. P. 1,885,653, Nov. 1, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1008. *British P.* 342,107, 1930; *Chem. Abs.*, 1931, 25, 4443. *French P.* 682,277, 1929; *Chem. Abs.*, 1930, 24, 4425.

<sup>137</sup> T. Midgley, C. A. Hochwalt and C. A. Thomas, U. S. P. 1,713,236, May 14, 1929, to General Motors Corp.; *Chem. Abs.*, 1929, 23, 3232.

<sup>138</sup> *British P.* 339,243, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2507. *French P.* 693,920, 1930.

<sup>139</sup> *British P.* 363,810, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 378. *French P.* 721,361, 1931; *Chem. Abs.*, 1932, 26, 4065.

<sup>140</sup> K. Schirmacher and L. van Zutphen, U. S. P. 1,838,234, Dec. 29, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1476. *French P.* 677,416, 1929. *German P.* 522,090, 1928; *Chem. Abs.*, 1931, 25, 3199.

<sup>141</sup> *British P.* 357,488, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 6183. *French P.* 691,662, 1930; *Chem. Abs.*, 1931, 25, 1706.

<sup>142</sup> *British P.* 324,004, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1930, 385. *French P.* 658,652, 1928, and addn. 38,127, 1930; *Chem. Abs.*, 1929, 23, 5352; 1931, 25, 5596.

<sup>143</sup> *British P.* 333,872, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 710.

<sup>144</sup> O. Schmidt, *German P.* 572,746, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4439. *British P.* 337,019, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1931, 148. *French P.* 688,593, 1930; *Chem. Abs.*, 1931, 25, 710. Also *British P.* 337,460, 1929; *Brit. Chem. Abs. B.*, 1931, 195.

<sup>145</sup> *British P.* 283,841, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1929, 485.

<sup>147</sup> *British P.* 308,755, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1929, 991.

<sup>148</sup> *British P.* 326,869, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1930, 521. *French P.* 678,305, 1929.

- (4) A cyclic diether such as dioxane.<sup>149</sup>
- (5) Twenty per cent of a low-boiling aliphatic ether such as dimethyl, diethyl, or methyl ethyl ether.<sup>150</sup>
- (6) Less than 5 per cent of saturated simple ethers such as diethyl, diamyl, or diisobutyl ether.<sup>151</sup>
- (7) Aldehydes, ketones or saturated and unsaturated acyclic or cyclic acetals, or acetals from 1,2- and 1,3-glycols.<sup>152</sup>
- (8) Up to 20 per cent of an organic compound unattacked by sodium but capable of replacing sodium by hydrogen in sodium triphenylmethyl, e.g., dioxane, furan, thiophene, acrylonitrile, phenylacetone. The presence of an unsaturated ether such as vinyl ethyl ether is also desirable.<sup>153</sup>
- (9) Up to 1 per cent of organic halogen compounds, such as ethylene dichloride, vinyl chloride, benzyl chloride, 1,2-dibromocyclohexane, 3-chloroquinoline or 1-chloronaphthalene.<sup>154</sup>

**Other Methods of Polymerization.** Anhydrous halides of the amphoteric elements, including the tetrahalides of tin and titanium, the tri- and pentahalides of antimony, boron chloride, halides of arsenic, iron and bismuth, as well as certain strongly negative substances such as sulphuryl chloride, phosphorus pentoxide, and phosphorus oxychloride have been suggested by Staudinger and Bruson<sup>155</sup> to polymerize diolefin hydrocarbons to give rubber-like products. Treatment of isoprene in benzene solution in the cold with stannic chloride yields a white rubber-like mass, soluble in benzene. This, together with the white powdery polymer of 1-phenylbutadiene, and the white rubbery polymer of cyclopentadiene can be vulcanized with sulphur chloride or they can be used in the preparation of lacquers.

A two-stage polymerization process, combining both the "sodium" and "emulsion" methods for preparing rubbery polymers, has been proposed.<sup>156</sup> For example, isoprene is partially polymerized with sodium at 35°C. Additional isoprene is incorporated and the mixture is emulsified with sodium oleate. The final polymerization is carried out at 60°C. Other stepwise processes have been used in which the method of polymerization does not change.<sup>157</sup>

Plauson<sup>158</sup> produced soluble rubber-like materials by polymerizing diolefins in mixture with drying oils in the presence of zinc chloride or aluminum chloride at ordinary or higher temperatures. Gerke<sup>159</sup> obtained synthetic rubber-polymers by treating a 1,3-diolefin with an inorganic peroxide (barium peroxide) and an organic acid anhydride (acetic anhydride). Butadiene may be polymerized by heating under increased pressure in the presence of oxygen and anhydrous organic solvents, e.g., tetrahydrostyrene, benzene or toluene. The resulting solution of

<sup>149</sup> G. Ebert and F. A. Fries, U. S. P. 1,832,450, Nov. 17, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1157. German P. 520,104, 1929; *Chem. Abs.*, 1931, 25, 2878. British P. 334,184, 1929; *Brit. Chem. Abs. B*, 1930, 1103. French P. 688,790, 1930.

<sup>150</sup> British P. 339,185, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2597. French P. 686,980, 1929; *Chem. Abs.*, 1931, 25, 845.

<sup>151</sup> E. Tschunker and W. Bock, U. S. P. 1,859,686, May 24, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3960. German P. 575,371, 1933; *Chem. Abs.*, 1933, 27, 3638.

<sup>152</sup> G. Ebert, F. A. Fries and P. Garbsch, German P. 532,455, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 337. British P. 340,008, 1929; *Brit. Chem. Abs. B*, 1931, 333. French P. 695,441, 1930; *Chem. Abs.*, 1931, 25, 2877. G. Ebert and P. Garbsch, U. S. P. 1,953,468, Apr. 3, 1934; *Chem. Abs.*, 1934, 28, 3939.

<sup>153</sup> G. Ebert, F. A. Fries and P. Garbsch, German P. 575,439, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3638. British P. 340,474, 1929; *Chem. Abs.*, 1931, 25, 5056. French P. 695,299, 1930; *Chem. Abs.*, 1931, 25, 2877. German P. 592,096, 1934; *Chem. Abs.*, 1934, 28, 2947.

<sup>154</sup> G. Ebert, F. A. Fries and P. Garbsch, U. S. P. 1,921,867, Aug. 8, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5339. German P. 524,668, 1929; *Chem. Abs.*, 1931, 25, 4370. British P. 347,902, 1930; *Brit. Chem. Abs. B*, 1931, 917. French P. 702,784, 1930; *Chem. Abs.*, 1931, 25, 4443.

<sup>155</sup> H. Staudinger and H. A. Bruson, U. S. P. 1,720,929, July 16, 1929; *Chem. Abs.*, 1929, 23, 4228. British P. 307,308, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 873. French P. 36,590, 1929, addn. to 665,537; *Chem. Abs.*, 1930, 24, 6065. French P. 695,745, 1930; *Chem. Abs.*, 1931, 25, 2878.

<sup>156</sup> British P. 335,616, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1930, 1122. British P. 302,738, 1927; *Brit. Chem. Abs. B*, 1930, 521.

<sup>157</sup> H. Plauson, German P. 361,429, 1917; *J.S.C.I.*, 1923, 42, 366A; *Kunststoffe*, 1922, 21, 176.

<sup>158</sup> F. H. Gerke, U. S. P. 1,834,186, Apr. 19, 1932, to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, 26, 3407.

polymers may be used in the manufacture of adhesives or coating and binding compositions.<sup>100</sup>

Methods have been described whereby the synthesis of diolefins and their subsequent polymerization to rubber-like polymers may be carried out in one operation.<sup>101</sup> For example, ethylene and acetylene and an added inert gas are heated in an autoclave under a pressure of 55-60 atmospheres at 350-400°C. The 1,3-butadiene so formed polymerizes when the reaction is performed in the presence of an alkali metal. Highly plastic masses resembling rubber are formed by heat-polymerizing butadiene hydrocarbons in the presence of unsaturated ketones.<sup>102</sup>

The polymerization of diolefins is catalyzed by small amounts of the carbonyls of heavy metals, e.g., those of iron, nickel, cobalt, molybdenum, tungsten and chromium. Isoprene is converted into a rubber-like mass by warming with 2 per cent of iron carbonyl in a current of air. Nickel carbonyl or iron carbonyl added with chromium propylnaphthalenesulphonate to a paint of polymerized butadiene in toluene accelerates the hardening of the film.<sup>103</sup>

According to Bysov<sup>104</sup> the polymerization of diolefins to synthetic rubbers is favored by the presence of (1) the dimer of the diolefin, which suppresses further undesirable formation of oily polymers, and (2) mixtures of substances capable of existing in tautomeric forms, such as ethyl benzoylacetate with diazoaminobenzene or phenylthiocarbimide. Synthetic rubber-like materials have been prepared<sup>105</sup> by polymerization in successive stages. The polymerization is partially completed and then additional quantities of the same or a different hydrocarbon are added. For example, if butadiene or isoprene represents the initial material, a different compound such as 2,3-dimethylbutadiene may be added.

Bridgman and Conant<sup>106</sup> were successful in polymerizing to rubbery materials such unsaturated hydrocarbons as isoprene, 2,3-dimethyl-1,3-butadiene and styrene at pressures of 3000-12,000 atmospheres at room temperature. At 12,000 atmospheres, isoprene yielded a tough, transparent, rubber-like solid which was 100 per cent polymerized. The reaction time is much less than can be obtained by any other method of polymerization, being 50 hours in this instance. Styrene, when subjected to pressure, yielded a hard resin, but when mixed with an equal part of malonic ester and subjected to 12,000 atmospheres, a soft, white, rubbery mass resulted. Vinyl acetate was also completely polymerized to a transparent rubber-like solid at high pressures.

In order to separate a mixture of olefins into monolefins and diolefins, Brooks<sup>107</sup> treated the mixture with a dispersion of finely divided cuprous chloride in aqueous ammonium chloride. The cuprous chloride reacts with the diolefins but not with the monolefins so that the two are easily separated. The diolefins are regenerated by heating and can then be polymerized to a rubber-like material.

<sup>100</sup> British P. 363,348, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 272.

<sup>101</sup> H. Plauson, U. S. P. 1,436,819, Nov. 28, 1922; *Chem. Abs.*, 1923, 17, 771. British P. 115,116, 1920, to H. O. Traun's Forschungslab. G. m. b. H.; *J. S. C. I.*, 1922, 41, 436A.

<sup>102</sup> K. Meisenburg, U. S. P. 1,901,354, Mar. 14, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3113. British P. 349,976, 1931; *Chem. Abs.*, 1932, 26, 5453. French P. 709,637, 1931; *Chem. Abs.*, 1932, 26, 1476.

<sup>103</sup> O. Ambrose and H. Reindel, German P. 523,033, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3358. British P. 340,064, 1929; *Chem. Abs.*, 1931, 25, 2878. See also O. Ambrose, J. Eisle and J. Stoeckel, U. S. P. 1,891,203, Dec. 13, 1932; *Chem. Abs.*, 1933, 27, 1893.

<sup>104</sup> B. W. Bysov, British P. 314,932 and 314,933, 1928; *Brit. Chem. Abs.* B, 1929, 829. Russian P. 11,276, 1929; *Chem. Zentr.*, 1931, 1, 3407; both to Gosudarstvennyi Trest Resinovoii Promyshlennosti (State Resinotrest).

<sup>105</sup> British P. 307,308, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 5352. British P. 335,616, 1929; *Chem. Abs.*, 1931, 25, 1706.

<sup>106</sup> P. W. Bridgman and J. B. Conant, U. S. P. 1,952,116, Mar. 27, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3415. *Cf. Proc. Nat. Acad. Sci.*, 1929, 15, 680; *Chem. Abs.*, 1929, 23, 5090. See also French P. 699,555, 1930; *Chem. Abs.*, 1931, 25, 3358. British P. 365,102, 1929, to Imperial Chemical Ind., Ltd.; *Chem. Abs.*, 1933, 27, 1643.

<sup>107</sup> B. T. Brooks, U. S. P. 1,988,479, Jan. 22, 1935, to Standard Alcohol Co.; *Chem. Abs.*, 1935, 29, 1684.



## VISCOUS OR OILY POLYMERS OF BUTADIENES

Reference has already been made to the oily by-products obtained during the polymerization of 1,3-diolefins to rubber-like materials. Highly viscous oils have been obtained by heating butadiene or its methyl derivative to 220°C. under pressure. However, if the temperature is not allowed to exceed 150°C. clear oils result. Polymers procured in this manner are recommended as constituents of paints, varnishes and adhesives.<sup>168</sup> Oily polymers are also prepared<sup>169</sup> by treating butadiene and its homologues at high temperatures and at ordinary pressures in the presence of nickel, aluminum, glass wool, silica gel, or spongy iron. It is said that in general butadiene and other olefins, obtained from the destructive distillation of coal, may be polymerized to yield products useful as lubricating oils and plastics.<sup>170</sup>

By heating a mixture of butadiene, benzene, ligroin and xylene at 180°C. and under 80 atmospheres for 4 hours, a polymerized product said to be of value in the preparation of transparent lacquers is formed.<sup>171</sup> Oils for varnishes are made by heating butadiene and similar hydrocarbons to 120-180°C. under pressure in the presence of oxygen or gases containing, or yielding, oxygen.<sup>172</sup> For coating and adhesive compositions the oily polymerization products of diolefins are used in admixture with cellulose derivatives or synthetic resins, along with various fillers.<sup>173</sup>

Resinous, non-rubber-like products result on heating diolefins with substantial quantities (e.g., 1 to 5 parts) of an inorganic acid, preferably of sulphur or phosphorus, or an organic derivative such as benzenesulphonic acid.<sup>174</sup> However, branched-chain olefins if polymerized at -10°C. in the presence of boron trifluoride, aluminum chloride or similar inorganic halides yield viscous, semi-solid products. The estimated molecular weights of these polymers range from 1000 to 10,000.<sup>175</sup>

Products of varying degrees of usefulness have been obtained<sup>176</sup> by separating the fractions resulting from the polymerization of butadiene hydrocarbons. Separation is effected by selective solvent action. For example, one fraction is recommended for use in the manufacture of artificial silk and another for coatings or impregnation of paper. Fractions are also obtained having the requisite properties necessary for vulcanization to synthetic rubber. Hard flexible foils, as exemplified in films, bands and lacquer coatings, possessing considerable resistance to chemical influences have been prepared by subjecting a non-distillable polymerization product of a diolefin to heat treatment in the presence of oxygen.<sup>177</sup> Similar materials are prepared by using sulphurizing agents instead of oxygen.<sup>178</sup>

## POLYMERIZATION OF CYCLIC 1,3-DIOLEFINS

Like the simple straight-chain conjugated diolefins, the cyclic diolefins, cyclopentadiene and 1,3-cyclohexadiene also possess a great tendency to polymerize to

<sup>168</sup> J. Eisele and J. Stöhrel, German P. 539,589, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2333. Also addn P. 540,998, 1928; *Chem. Abs.*, 1932, 26, 2333. British P. 328,908, 1928, *Brit. Chem. Abs. B.*, 1930, 754. French P. 679,539, 1929; *Chem. Abs.*, 1930, 24, 3914.

<sup>169</sup> French P. 683,284, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 4519.

<sup>170</sup> British P. 305,603, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1929, 275.

<sup>171</sup> J. Stöhrel and J. Eisele, German P. 542,805, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3124.

<sup>172</sup> French P. 39,353, 1930, addn. to 679,539, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2333.

<sup>173</sup> British P. 359,944, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4144.

<sup>174</sup> British P. 238,152, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1931, 261.

<sup>175</sup> British P. 401,297, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1934, 136.

<sup>176</sup> French P. 691,901, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1346.

<sup>177</sup> O. Schmidt, U. S. P. 1,901,045, Mar. 14, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3113. British P. 329,000, 1929; *Chem. Abs.*, 1930, 24, 5536. French P. 683,990, 1929; *Chem. Abs.*, 1930, 24, 1753.

<sup>178</sup> O. Schmidt, German P. 568,906, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2845.

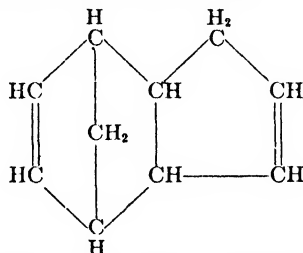
high-molecular-weight resinous polymers. These products, however, differ somewhat from the rubber-like polymers of butadiene and isoprene.

**Cyclopentadiene.** By polymerization under controlled conditions, cyclopentadiene has been shown to yield a whole series of lower polymers, including the dimer, trimer, tetramer, and pentamer, as well as a complex polycyclopentadiene  $(C_5H_6)_x$ , where  $x$  may vary within the limits 20-100. The polymerization of cyclopentadiene<sup>179</sup> to solid polymers proceeds spontaneously on standing at ordinary temperature, particularly in the presence of air or oxygen, but is more rapid at higher temperatures.<sup>180</sup> Light has little influence on the reaction.<sup>181</sup> However when small amounts of ethyl mercaptan are added to the cyclopentadiene, resin-formation takes place upon standing in light.<sup>182</sup> By heating cyclopentadiene to 135°C., dicyclopentadiene<sup>183</sup> is formed mainly, but by prolonging the heat treatment and employing higher temperatures other polymers can be obtained.<sup>184</sup> These polymers are crystalline solids (up to the pentamer, at least) and can be separated from one another by vacuum distillation. Each polymer contains two double bonds and can be hydrogenated to the corresponding dihydro- and tetrahydro derivatives. By thermal treatment they can be partially depolymerized with the formation of cyclopentadiene and its lower polymers. The melting points of the lower polymers of cyclopentadiene are given in Table 23.

TABLE 23.—Polymers of Cyclopentadiene.

Compound	Melting Point °C.
Dicyclopentadiene . . . .	{ 32.5 (α-form) 19.5 (β-form)
Tricyclopentadiene . . . .	60
Tetracyclopentadiene . . . .	188-190
Pentacyclopentadiene . . . .	270
Polycyclopentadiene . . . .	decomposes above 300

The chemical constitution of these crystalline polymers has not been definitely decided. Wieland<sup>185</sup> proposed a formula which assumes the addition of a cyclopentadiene molecule activated in the 1,4 position to another molecule at the 1,2 position. The investigations of Alder and Stein<sup>186</sup> tend to corroborate this formula which may be represented by the graphic structure



<sup>179</sup> In the case of the spontaneous polymerization of cyclopentadiene to its dimer the reaction is practically independent of the presence of oxygen. See G. R. Schultze, *JACS*, 1934, 56, 1552.

<sup>180</sup> H. E. Roscoe, *JCS*, 1885, 47, 669; *Ann.* 1886, 232, 348; *Chem. Zentr.*, 1886, 449. A. Etard and P. Lambert, *Compt. rend.*, 1891, 112, 945; *JCS*, 1891, 60, 1085. A. Kronstein, *Ber.*, 1902, 35, 4150. H. Stobbe and F. Dünhaupt, *Ber.*, 1919, 52, 1436. A. P. Terent'ev and L. A. Solokhin (*Sintet. Kauchuk*, 1933, 5, 9; *Chem. Abs.*, 1934, 28, 3385) report that the reaction between cyclopentadiene and p-nitrobenzene-diazonium chloride can be utilized to determine the extent of polymerization.

<sup>181</sup> H. Stobbe and F. Reuss, *Ann.*, 1912, 391, 151; *Chem. Abs.*, 1912, 6, 3275.

<sup>182</sup> O. Kruber and W. Schade, *Brennstoff-Chem.*, 1933, 14, 124; *Chem. Abs.*, 1933, 27, 3802.

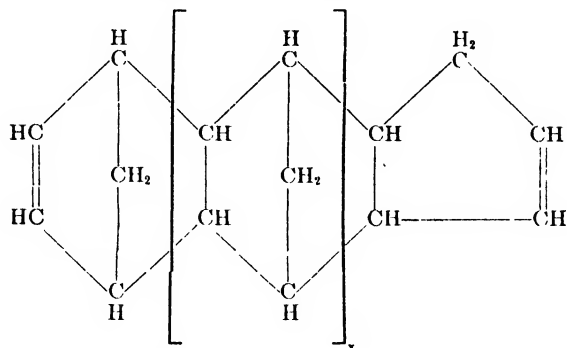
<sup>183</sup> Crystalline dicyclopentadiene has been obtained from coke-oven gas in amounts of 15-20 kg. per 1000 tons of coal. See R. Horclois, *Chimie et industrie*, 1934, 33 (April Spec. No.), 357; *Chem. Abs.*, 1935, 29, 140.

<sup>184</sup> H. Staudinger and A. Rheiner, *Helv. Chim. Acta*, 1924, 7, 23; *Chem. Abs.*, 1924, 18, 1275. H. Staudinger and H. A. Bruson, *Ann.*, 1926, 447, 97; *Chem. Abs.*, 1926, 20, 2148. H. A. Bruson and H. Staudinger, *Ind. Eng. Chem.*, 1926, 18, 881.

<sup>185</sup> H. Wieland, *Ber.*, 1906, 39, 1492.

<sup>186</sup> K. Alder, G. Stein, and others, *Ann.*, 1932, 496, 204; 1933, 504, 216; *Brit. Chem. Abs.*, 1932, 988; *Chem. Abs.*, 1933, 27, 5811. *Ber.*, 1934, 67, 813; *Chem. Abs.*, 1934, 28, 6114. *Angew. Chem.*, 1934, 47, 837; *Chem. Abs.*, 1935, 29, 2516.

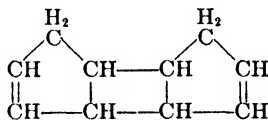
Furthermore, the latter investigators assert that the lower polymers of cyclopentadiene form an homologous series of the general formula



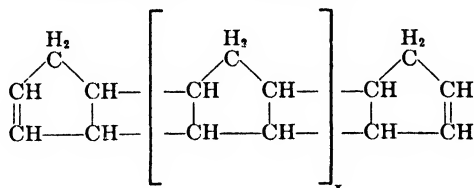
in which  $x$  is a small integer.

Additional corroboration for the Wieland formula has been made available through the researches of Pirsch<sup>187</sup> on the molecular depression of the melting point. The argument is based on observations that dicyclic compounds, whose molecular structure is almost equally developed in all three spatial directions, have very high values for molecular melting point depressions.<sup>188</sup> The results obtained with  $\alpha$ -dicyclopentadiene were in accord with this view.

An alternative formula for the structure of dicyclopentadiene was originally advanced by Kraemer and Spilker.<sup>189</sup> If 1,2 addition takes place the dimer may be represented by the graphic formula



This formula is supported by Staudinger and Rheiner<sup>190</sup> who assign to the non-resinous polymers of cyclopentadiene the constitution



where  $x$  is a relatively small integer.

**Polycyclopentadiene.** Products very different from the simple crystalline polymers described in the preceding section are obtained when cyclopentadiene is subjected to the action of various strong polymerizing agents, the best being stannic chloride and antimony pentachloride. Boron trichloride, titanium tetrachloride, arsenic halides, ferric and bismuth halides, sulphuryl chloride, phosphorus pentoxide

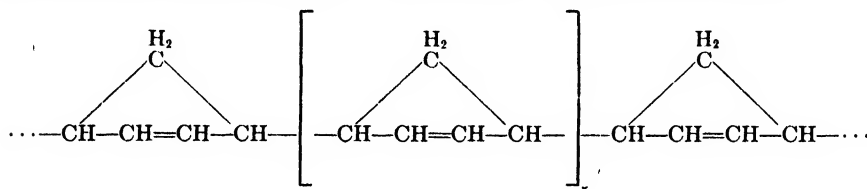
<sup>187</sup> J. Pirsch, *Ber.*, 1934, 67, 101; *Brit. Chem. Abs.*, A, 1934, 285.

<sup>188</sup> K. Alder and G. Stein (*Ber.*, 1934, 67, 373; *Chem. Abs.*, 1934, 28, 3061) are of the opinion that molecular melting point depressions are of limited value in the determination of configuration in the case of cyclopentadiene polymers. It is pointed out that both configurations, under question, are capable of existing in stereoisomeric forms; hence either of the proposed formulas is capable of fulfilling the conditions for high molecular melting point depressions.

<sup>189</sup> G. Kraemer and A. Spilker, *Ber.*, 1896, 29, 552; *J.C.S.*, 1896, 70 (1), 289.

<sup>190</sup> H. Staudinger and A. Rheiner, *loc. cit.*

and phosphorus pentachloride exert a somewhat less vigorous polymerizing action. With stannic chloride the reaction is so vigorous that strong cooling in conjunction with an inert liquid diluent must be employed. The product in every case is a white amorphous powder somewhat resembling rubber. However the resin obtained by polymerizing dicyclopentadiene with heat and pressure is quite hard and resembles amber.<sup>101</sup> The rubber-like polymers are insoluble in acetone, ether and alcohol, although colloidal solutions are formed with common rubber solvents. When dried at 50°C. in a high vacuum the polymer swells to a spongy brittle white mass which can be powdered. Polymerized cyclopentadiene has an empirical composition corresponding to  $(C_5H_6)_x$  and a molecular weight which varies between about 1260 and 6670. The pure compound is unsaturated and contains one double bond per  $C_5H_6$  unit. It appears that polycyclopentadiene, or "cyclopentadiene rubber," consists of a series of hydrocarbons of the general formula:<sup>102</sup>



in which x is an integer varying from about 20 to 100.

When exposed to air, cyclopentadiene rubber gradually takes up oxygen to the extent of about 19.5 per cent by weight to give a deep-orange powder of the composition  $(C_5H_6O)_x$ . Polycyclopentadiene can also be vulcanized with sulphur chloride in chloroform solution to yield products varying from a soft gel to a hard-rubber ebonite material, which can be pulverized only with great difficulty. All these vulcanized products are insoluble in organic solvents.

Polycyclopentadiene is attacked by ozone, nitrogen trioxide, and hydrogen chloride, and can be hydrogenated to a brown, glassy, insoluble mass. According to Bruson and Staudinger,<sup>100</sup> polycyclopentadiene might find application as a lacquer base rather than as a rubber substitute.

Gum-like modifications of polycyclopentadiene have been found in appreciable quantities in mains for the distribution of coke-oven gas and carburetted water-gas. The formation of such gummy and resinous polymers presents a serious problem with regard to clogging of meters and small pipes. Shively suggested<sup>104</sup> that the polymerization of dienes in the pipe-lines was promoted by the presence of traces of oxygen and favored by high pressures and humidities. An explanation for the effect of oxygen and pressure is afforded by the alternative view<sup>103</sup> that resinification takes place as a result of the vapor-phase condensation of the unsaturated hydrocarbon with nitrogen peroxide and the subsequent polymerization of the condensation products. The nitrogen peroxide is formed by the oxidation of nitric oxide which is unavoidably introduced into the gas during its manufacture. (See Chapter 35.)

**1,3-Cyclohexadiene.** This hydrocarbon is more resistant to polymerization than butadiene or its 2- and 3-alkyl derivatives and is more related, in this respect, to the 1- and 4-substituted butadienes. It is not acted upon by sodium. Con-

<sup>101</sup> L. Gurwitsch, "Wissenschaftliche Grundlagen der Erölbearbeitung;" Julius Springer, Berlin, 1913, 48.

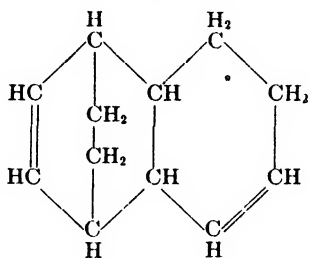
<sup>102</sup> H. A. Bruson and H. Staudinger, *Ind. Eng. Chem.*, 1926, 18, 331.

<sup>103</sup> H. A. Bruson and H. Staudinger, *loc. cit.*

<sup>104</sup> W. L. Shively, *Am. Gas Assoc. Proc.*, 1931, 13, 765; *Chem. Abs.*, 1932, 26, 4159.

<sup>105</sup> G. Berkhoff, *Het Gas*, 1931, 51, 460; *Chem. Abs.*, 1932, 26, 1755. P. Schuftan, *Brennstoff-Chem.*, 1932 13, 104; *Chem. Abs.*, 1932 26, 2849. See also A. L. Ward, C. W. Jordan and W. H. Fulweiler, *Ind. Eng. Chem.*, 1932, 24, 969.

concentrated sulphuric acid reacts explosively with it to yield resins or tars.<sup>196</sup> Anhydrous metallic halides such as ferric chloride and aluminum chloride<sup>197</sup> convert it into resins. On heating at 200-220°C. for several hours, the hydrocarbon is largely polymerized with the production of a solid rubber-like polymer ("dihydrobenzene rubber") and a terpenic dimer. Practically no polymerization occurs on heating cyclohexadiene below about 120°C. The dimer of cyclohexadiene is a liquid which is resinified by concentrated sulphuric and nitric acids. Hofmann and Damm<sup>198</sup> have assigned the following formula to dicyclohexadiene:



This structure has been confirmed by Alder and Stein.<sup>199</sup>

Useful resins are said to be obtained by treatment of cyclohexadiene with polymerizing agents in the presence of diluents.<sup>200</sup> Thus, 200 parts of cyclohexadiene, 500 parts of glacial acetic acid and 5 parts of 97 per cent sulphuric acid are boiled for 7 hours, the acetic acid removed by vacuum distillation and the sulphuric acid by washing with water and mild alkali. The product is a clear, glassy solid which is soluble in turpentine or benzene. Aluminum chloride has also been suggested as a polymerizing agent. For instance, 6 parts of anhydrous aluminum chloride are slowly added, with cooling, to 30 parts of cyclohexadiene, and the mixture is heated at 40°C. until reaction ceases. The mass is extracted with benzene, the extract washed with soda solution and the benzene distilled off to yield a colorless resin. Alternatively, the reaction mixture is washed with dilute hydrochloric acid and the resin distilled with steam. In a similar way, resins may be prepared from 1-methyl-1,3-cyclohexadiene.

A thick, amber-yellow resinous substance was obtained by Zelinsky and Titova<sup>201</sup> by allowing 1,3-cyclohexadiene to absorb oxygen to the limit of its capacity. The analysis indicated that the product contained 1 mol of oxygen per mol of cyclohexadiene and in view of its resinous nature, a dimeric formula,  $C_{12}H_{16}O$ , has been suggested.

#### Co-POLYMERIZATION OF DIOLEFINS

Synthetic resins are now being prepared by the condensation of diolefins with olefins in cracked-gasoline fractions under the influence of aluminum chloride. Several reactions occur in this treatment, including polymerization of the diolefin, condensation of the diolefin with a monoolefin, and condensation of diolefins with

<sup>196</sup> A. Baeyer, *Ber.*, 1892, 25, 1841.

<sup>197</sup> N. D. Zelinsky, Y. I. Denisenko, M. S. Eventova and S. I. Khromov (*Sintet. Kauchuk*, 1933, 4, 11; *Chem. Abs.*, 1934, 28, 3617) found that 1,3-cyclohexadiene polymerized when heated with aluminum chloride and that 1,4-cyclohexadiene was partially polymerized and partially dehydrogenated to benzene.

<sup>198</sup> F. Hofmann and P. Damm, *Mitt. Schlesischen Kohlenforach, Kaiser-Wilhelm Ges.*, 1925, 2, 97; *Chem. Abs.*, 1928, 22, 1249.

<sup>199</sup> K. Alder and G. Stein, *Ann.*, 1932, 496, 197; *Chem. Abs.*, 1932, 26, 5093.

<sup>200</sup> British P. 23,543, 1912, to Badische Anilin & Soda-Fabrik; *J.S.C.I.*, 1913, 32, 876. German P. 263,159, 1912; *Chem. Abs.*, 1914, 8, 266.

<sup>201</sup> N. D. Zelinsky and A. N. Titova, *Ber.*, 1931, 64, 1399; *Chem. Abs.*, 1931, 25, 4235.

aromatic hydrocarbons. The two latter reactions both give rise to hard resins under appropriate conditions.

**Condensation of Diolefins with Monolefins.** When anhydrous aluminum chloride is placed in pure isoprene, no temperature rise occurs and there is no appreciable reaction, though a small amount of insoluble polymer is formed on long standing. If, however, a small amount of a monoolefin hydrocarbon, such as 2-pentene or trimethylene, is introduced into this mixture a vigorous reaction takes place immediately. Certain phases of this interesting reaction were investigated and discussed by Aschan.<sup>202</sup> Later, Thomas and Carmody<sup>203</sup> investigated the products of the reaction between 2-pentene and isoprene in the presence of aluminum chloride at 1-4°C. After decomposition of the reaction mixture with water, two types of product were obtained, namely, an insoluble polymer approximating in composition to  $(C_6H_8)_x$ , and a soluble polymer, ranging from a viscous

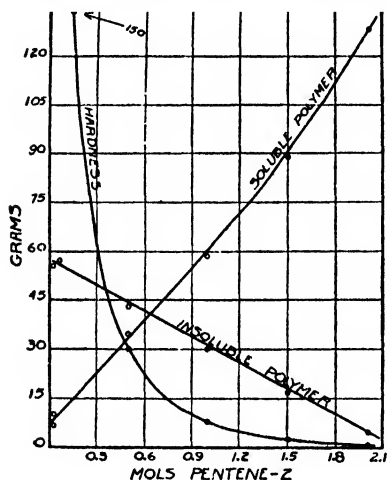


FIG. 48.  
Relationship Between Two Polymers as 2-Pentene is Added to Isoprene. (C. A. Thomas and W. H. Carmody)

Courtesy Industrial and Engineering Chemistry

oil to a hard resin. The relative proportions of these two products and also the hardness of the soluble polymer depended upon the proportions of 2-pentene and isoprene employed. The amount of soluble polymer increased and its hardness diminished with increasing proportions of 2-pentene. Only small amounts of soluble polymer (and large amounts of insoluble polymer) were formed with small proportions of 2-pentene. (See Fig. 48.) Subsequent experiments have indicated that 2-pentene produces this effect by acting as a mutual solvent for the isoprene and the aluminum chloride.<sup>204</sup>

The soluble polymer, which is of technical interest, consists of a mixture of higher oils and a hydrocarbon resin, the hardness depending upon the amount of oils present. The resin is soluble in most hydrocarbon solvents and drying oils. On exposure in thin films to air, the resin slowly oxidizes, becoming harder. The insoluble polymer, on the other hand, is a white granular material, which tends to depolymerize at 116°C. This material is probably a true polymer of isoprene.

The application of these observations to the manufacture of a synthetic resin, which may find use in the paint and varnish industries, has been described by Thomas and Carmody.<sup>205</sup> A cracked-gasoline distillate containing diolefins, mono-

<sup>202</sup> O. Aschan, *Översigt Finska Vetenskaps Soc.*, 1915, 58, 122; *Chem. Abs.*, 1916, 14, 3654.

<sup>203</sup> C. A. Thomas and W. H. Carmody, *J.A.C.S.*, 1932, 54, 2480.

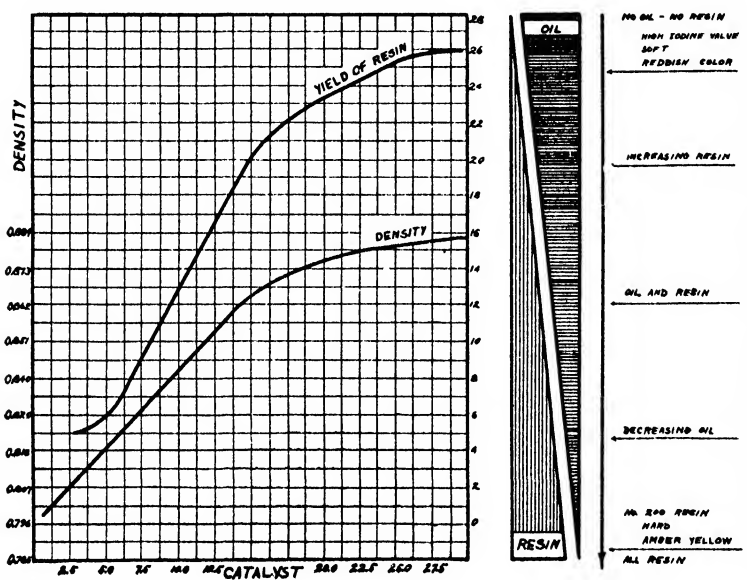
<sup>204</sup> C. A. Thomas and W. H. Carmody, *J.A.C.S.*, 1933, 55, 3854.

<sup>205</sup> C. A. Thomas and W. H. Carmody, *Ind. Eng. Chem.*, 1932, 24, 1125. C. A. Thomas and C. A.

lefins, and also aromatic hydrocarbons, is used as raw material.<sup>206</sup> The products of vapor-phase cracking are suggested. A fraction obtained at high temperature and low pressure with the following characteristics is mentioned by these investigators as having proved successful in the production of the resin:

Boiling range, °C.	23°-180°
Specific gravity at 20°C.	0.84-0.86
Aromatics, per cent	40-55
Unsaturates, per cent	45-60
Bromine number, milligrams per gram	1003
Refractive index	1.416-1.517
Average molecular weight	150

Polymerization is carried out in vessels equipped with cooling coils. Anhydrous aluminum chloride is added in a thin stream and towards the end of the reaction the



Courtesy Industrial and Engineering Chemistry

FIG. 49.—Effect of Catalyst on Density and Yield of Resin from Cracked Gasoline. (C. A. Thomas and W. H. Carmody.)

rate of addition may be somewhat increased. After a time a point is reached when no more heat is evolved. The distillate darkens in color as polymerization proceeds and the specific gravity increases 10 to 15 per cent. With increasing proportions of catalyst, the yield of resin rises to a maximum and its iodine value falls to a minimum. (See Figs. 49 and 50.) The effectiveness of the catalyst is believed to be proportional to the amount of it that goes into solution. About 6 hours is required for complete polymerization. After the completion of the polymerization the reaction mixture is treated with an alkali and the precipitated aluminum hydroxide and insoluble polymer are filtered off. The filtrate, consisting of a solution of the soluble resin, is first distilled under reduced pressure and then steam is passed directly into the molten resin. A diagram of the process for obtaining resins from petroleum distillates is given in Fig. 51. By controlling the time and temperature of the steam treatment, the hard-

Hochwalt, U. S. P. 1,836,029, Dec. 15, 1931, to Davton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1932, 26, 1144. British P. 340,001, 1929; *Chem. Abs.*, 1931, 25, 2887. See also A. D. Camp, *Chem. Met. Eng.*, 1934, 41, 123. M. Jeanny, *Rev. gen. mat. plastiques*, 1934, 10, 306. *Chem. Abs.*, 1934, 28, 7041.

<sup>206</sup> See B. V. Buizov (*J. Applied Chem.*, U. S. R., 1933, 6, 1074; *Chem. Abs.*, 1934, 28, 5711) for another description of rubber-preparation from petroleum.

ness of the resin can be varied within certain limits. The resulting resin may be used for various industrial purposes. For varnish making, a light-amber-colored, hard, brittle material, melting at 110-115.6°C. (ball and ring method), may be prepared. This resin is soluble in practically all hydrocarbon solvents, and all acetic acid esters except ethyl acetate. It also dissolves readily in drying oils, such as linseed oil and tung oil. With the latter drying oil the resin makes varnishes which dry quite rapidly.<sup>307</sup> The resin is insoluble in methanol, ethyl alcohol, ethyl acetate, and acetone. It is practically neutral and its iodine value can be varied to bring out unusual characteristics. For example, on baking a film, prepared from a highly unsaturated resin in petroleum solvents, at 105°C. for one hour, the film becomes insoluble in its original solvents. This phenomenon is comparable with the drying of unsaturated oils.

Later investigations<sup>308</sup> on preparation of resins from petroleum revealed that the nature of the final product can be varied by employing different proportions of two cracked-distillate fractions, one boiling at 25-50° and the other at 125-180°. It was also found that the insoluble polymer referred to above can be converted into a use-

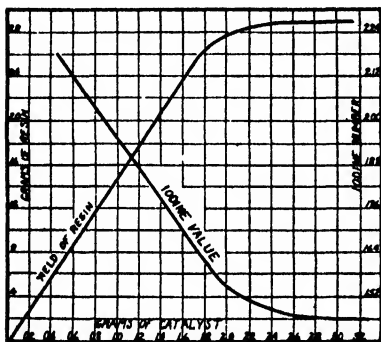


FIG. 50.

Relation of Iodine Number and Yield of Resin from Cracked Gasoline. Weights are expressed in grams per 100 cc. (C. A. Thomas and W. H. Carmody.)

Courtesy Industrial and Engineering Chemistry

ful resin. The filter residue is freed of inorganic matter (e.g., aluminum chloride) by repeated washings with hydrochloric acid (10 per cent). After this treatment there remains a white granular material insoluble in most solvents. By heating this mass at 300° out of contact with air a light amber-colored resin results which is soluble in drying oils and in benzene, gasoline and naphtha.

According to Schering,<sup>309</sup> oils and resins are formed by condensing diolefins (butadiene, isoprene, or dipentene) with monoolefin hydrocarbons (amylene, diamylene, menthene, pinene, camphene and styrene) in the presence of catalysts, e.g., anhydrous aluminum chloride, ferric chloride, boron trichloride, and magnesium chloride. Sodium stearate<sup>310</sup> has also been recommended as a catalyst for use in the polymerization of mixtures of butadiene hydrocarbons with monoolefin benzenes. Resinous materials were produced in this way by condensing butadiene and styrene. The products consist of an ether-soluble portion, a sticky solid, and an ether-insoluble yellow powder. Treatment of equal parts of camphene and isoprene with 5 per cent of aluminum chloride yielded an ether-soluble, soft solid and an insoluble residue, which was white or light yellow, easily pulverized and insoluble in most of the common solvents.

By condensation of a diolefin with styrene, rubber-like or plastic masses are obtained depending upon the proportions of the reactants. The polymerization

<sup>307</sup> C. A. Thomas and P. E. Marling, *Ind. Eng. Chem.*, 1932, 24, 871.

<sup>308</sup> C. A. Thomas and W. H. Carmody, U. S. P. 1,932,706, Dec. 4, 1934, to Dayton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1935, 29, 523.

<sup>309</sup> E. Schering, German P. 278,486, 1913, to Chem. Fabr. auf Actien, *J.S.C.I.*, 1915, 34, 238.

<sup>310</sup> E. Tschunkur and W. Bock, German P. 538,785, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2205.



is carried out, after emulsification with sodium stearate or sodium mono- or dibutynaphthalenesulphonate, at 40-60°C. for several days.<sup>211</sup> The rubber-like products may be vulcanized<sup>212</sup> and used in the manufacture of conveyor belts, tires, driving-belts and coatings. Instead of styrene, other olefin benzenes such as polyvinylbenzenes or nuclear or side-chain homologues of styrene may be used. For example, butadiene and  $\alpha$ -methylstyrene are polymerized in aqueous emulsion in the presence of diethylaminoethyloleamide at 60°C. for 4 to 5 days to yield a synthetic rubber.<sup>213</sup> A mixture of a diolefin and vinyl-naphthalene (not more than 50 per cent) may also be polymerized in a similar way to furnish a latex which is coagulated and may be vulcanized with the addition of fillers, e.g., lampblack.<sup>214</sup>

A material resembling rubber or deresinated gutta-percha, and capable of replacing rubber in the insulation of submarine cables, is prepared by polymerizing

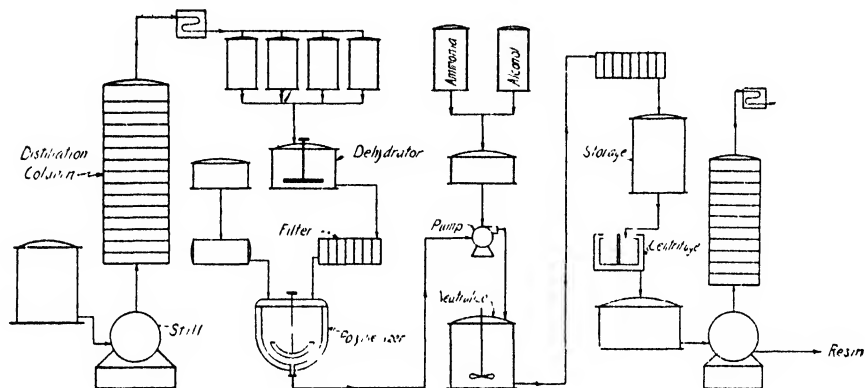


FIG. 51.—Schematic Representation of the Production of Resins by Treatment of Cracked Petroleum Distillates with Aluminum Chloride. (C. A. Thomas and W. H. Carmody.)

a mixture of a butadiene hydrocarbon and an aromatic olefin (styrene, naphthyl-ethylene, and divinylbenzene) at 20-200°C. in the presence of a catalyst, such as sodium or sodium amalgam, and, if necessary, of an antioxidant and a hydrocarbon swelling agent to render the product thermoplastic.<sup>215</sup> Similarly, polyolefinic benzene derivatives (e.g., styrene, divinylbenzene) may be mixed with a double proportion of butadiene and polymerized. However, in this case the reaction is carried out in any aqueous emulsion.<sup>216</sup>

**Condensation of Diolefins and Monoolefins with Aromatic Compounds.** Thomas and Carmody<sup>217</sup> have found that isoprene condenses with a number of benzene homologues in the presence of anhydrous aluminum chloride, yielding hard resins. Benzene homologues employed in the condensations included toluene, o-, m- and p-xylene, ethylbenzene, propylbenzene, isopropylbenzene, hexamethyl-

<sup>211</sup> British P. 339,255, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2598. E. Tschunkur and W. Bock, German P. 570,980, 1933; *Chem. Abs.*, 1933, 27, 4441.

<sup>212</sup> A. Beck and M. Mueller-Cunradi, German P. 573,569, 1933; *Chem. Abs.*, 1933, 27, 4442. K. Meisenburg and W. Bock, U. S. P. 1,915,745, June 27, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4440.

<sup>213</sup> British P. 342,314, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4443. French P. 701,102, 1930; *Chem. Abs.*, 1931, 25, 3876.

<sup>214</sup> British P. 358,877, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 6158. French P. 40,244, 1931, addn. to 701,102; *Chem. Abs.*, 1933, 27, 862. See also K. Meisenburg and W. Bock, German P. 573,569, 1933, addn. to 570,980, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4441.

<sup>215</sup> W. E. Hugh, British P. 345,939, 1929, to Standard Telephones & Cables, Ltd.; *Brit. Chem. Abs.* B, 1931, 710. French P. 707,692, 1930, to Le Material Telephonique S. A.; *Chem. Abs.*, 1932, 26, 734.

<sup>216</sup> French P. 699,154, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3521.

<sup>217</sup> C. A. Thomas and W. H. Carmody, *Ind. Eng. Chem.*, 1932, 24, 1123.

benzene, sec-butylbenzene, tert-butylbenzene and tert-amylbenzene. No appreciable amount of resin was obtainable in the condensation of isoprene with benzene. However, Thomas<sup>218</sup> prepared a resin by polymerizing a solution of impure dipentene in benzene using aluminum chloride as a catalyst. Hexadienes, butadienes and dimethylbutadiene as well as isoprene are suggested for resin manufacture with homologues of benzene and aluminum chloride. Other resins have been prepared by the reactions of various mixtures of olefins and diolefins with substituted benzenes.<sup>219</sup> Among these are the reaction of a substituted benzene with (A) a cyclic diolefin and an open-chain monolefin; (B) a cyclic olefin and a straight-chain diolefin and (C) a cyclic olefin and a cyclic diolefin. Aluminum chloride is employed as catalyst.

Michel<sup>220</sup> was able to alkylate naphthalene and its hydrogenated derivatives with ethylene or other olefins using ferric chloride or aluminum chloride as catalysts. Only products recommended as motor fuels or dye intermediates resulted when the reaction was carried out at pressures of 20-30 atmospheres and at temperatures up to 200°C. Upon subjecting anthracene, phenanthrene or acenaphthene to analogous treatment using slightly greater pressures, resins and lubricating oils were produced.<sup>221</sup>

The reaction of 14 parts of isoprene and 50 parts of toluene at 160°C. under 2-7 atmospheres pressure (sodium catalyst) yields 3-methyl-5-phenylpentene as an oily liquid (b.p., 218-222°) with an aromatic odor.<sup>222</sup> Similar condensations have been effected between butadiene and tetrahydronaphthalene, 2,3-dimethylbutadiene and toluene and between butadiene and toluene. Rubber-like masses are obtained in small amounts in these reactions.

Berry and Reid<sup>223</sup> obtained ethyl derivatives with ethylene, and propyl derivatives with propylene, when benzene, toluene, bromobenzene, and cyclohexane were treated with these olefins in the presence of aluminum chloride. Tarry high-boiling products were formed at the same time in varying amounts.

Condensation products of 1,3-butadiene and cyclic hydrocarbons having at least one aromatic nucleus and no olefinic sidechains, or alkyl, halogeno, nitro, alkoxy, or carbalkoxy derivatives, can be prepared,<sup>224</sup> employing a catalyst such as aluminum chloride. Thus 1,3-butadiene is passed into mixtures of aluminum chloride and tetrahydronaphthalene, benzene, m-xylene, chlorobenzene and nitrobenzene. The products are stated to be useful as thermohardening bases for lacquers. Besides aluminum chloride, boron fluoride, or anisolv-acids<sup>225</sup> derived from these halides, may be used as catalysts. Soft resins are prepared by heating car-

<sup>218</sup> C. A. Thomas, U. S. P. 1,939,932, Dec. 19, 1933; to Dayton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1934, 28, 1559. U. S. P. 1,947,626, Feb. 20, 1934; *Chem. Abs.*, 1934, 28, 2927.

<sup>219</sup> C. A. Thomas, U. S. P. 1,982,707, Dec. 4, 1934, to Dayton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1935, 29, 523.

<sup>220</sup> R. Michel, U. S. P. 1,766,344, June 24, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 4051. British P. 265,601, 1927; *Brit. Chem. Abs. B.*, 1928, 740. German P. 505,403, 1926, with addns. 523,691, 1926, and 523,834, 1927; *Chem. Abs.*, 1931, 25, 3667, 4282. See also U. S. P. 1,667,214, Apr. 24, 1928 and re-issue 17,548, Dec. 31, 1929; *Chem. Abs.*, 1928, 22, 1980; 1930, 24, 1123. British P. 273,665, 1927, and 295,990, 1928; *Brit. Chem. Abs. B.*, 1928, 740; 1930, 276.

<sup>221</sup> R. Michel, U. S. P. 1,741,478, Dec. 31, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1123. U. S. P. 1,878,963, Sept. 20, 1932; *Chem. Abs.*, 1933, 27, 310. German P. 550,494, 1927; *Chem. Abs.*, 1932, 26, 4065. See also British P. 316,951, 1929; *Brit. Chem. Abs. B.*, 1931, 194. French P. 665,402, 1928; *Chem. Abs.*, 1930, 24, 930.

<sup>222</sup> F. Hofmann and A. Michael, U. S. P. 1,934,123, Nov. 7, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 488. German P. 557,514, 1928; *Chem. Abs.*, 1933, 27, 514.

<sup>223</sup> T. M. Berry and E. E. Reid, *J.A.C.S.*, 1927, 49, 3142.

<sup>224</sup> British P. 338,109, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2313. British P. 315,315, 1929; *Brit. Chem. Abs. B.*, 1930, 1103.

<sup>225</sup> In extension of Werner's so-called "anhydro-acids," neutral molecules which combine with a solvent increasing its acidity by forming complex anions are called "anisolv acids." For example, when more than 1 mol of zinc chloride is present in a complex acid, the anion is regarded as the co-ordination center. Many other compounds such as magnesium chloride, zinc chlorate, sulphur dioxide, boron trioxide and pyroboric acetate increase the ionization of organic acids. Boron trifluoride is the most strongly acting anisolv-acid. Boron trifluoride-acetic acid boiling at 60°C. under 13 mm. pressure is as strong as sulphuric acid. H. Merwein, *Ann.*, 1927, 455, 227; *Brit. Chem. Abs.*, 1927, 886.

bazole with olefins at 100-200°C. in the presence of aluminum chloride, fuller's earth, tonsil, or franconite. For optimum results, the use of an inert solvent is said to be desirable.<sup>226</sup> The residue resulting from the refining of oils with liquid sulphur dioxide has been treated with olefins in the presence of aluminum chloride to produce a yellow oil and a resinous product.<sup>227</sup>

### VULCANIZATION OF RUBBER-LIKE POLYMERS

Vulcanizing procedures involving the use of sulphur alone have not, as yet, been successful in converting the polymerization products of butadiene and its homologues into finished synthetic rubber of good strength and elasticity. However, the incorporation of finely divided substances such as carbon, colloidal silicic acid or oxides of metals with the polymerization product materially increases the quality of the resulting vulcanized material.<sup>228</sup> Tschunkur and Bock<sup>229</sup> were successful in obtaining a synthetic rubber of good tensile strength and extensibility by vulcanizing stocks containing 30-80 per cent of their weight in carbon black. The tensile strength is reported as 150-275 kg. per sq. cm. with an ultimate elongation of 400 to 800 per cent. The tensile product (kg./sq. cm.  $\times$  % stretch) ranged from 50,000 to 190,000. On the other hand, vulcanization in the absence of carbon black gave products having a tensile product of only 15,000 to 40,000. The same workers have reported<sup>230</sup> that a synthetic rubber of good quality resulted when a mixture containing 45 per cent of polymerized styrene and 55 per cent of butadiene polymerizate was vulcanized with finely divided carbon comprising 20-70 per cent of the weight of the mixture. Polymerization products of vinyl-naphthalene have been suggested for use in an analogous manner with butadiene polymers. Products with a tensile strength of 30 to 50 kg. per sq. cm. and an ultimate elongation of 300 to 500 per cent have been obtained<sup>231</sup> by vulcanizing a polymerization product of butadiene and isoprene with 15 parts of zinc oxide, 3 parts of sulphur, 2 parts tar and 1 part diphenylguanidine. However, when the vulcanization was carried out with the addition of 50 parts of carbon black, the tensile strength ranged from 180 to 220 kg. per sq. cm. and the ultimate elongation had increased to 600-800 per cent. Similarly, a polymerization mixture prepared from a 10:3 mixture of butadiene and  $\alpha$ -methylstyrene<sup>232</sup> was compounded with 50 parts carbon black, 15 parts zinc oxide, 2 parts stearic acid, 1 part sulphur, 1.77 parts of an accelerator and vulcanized. The product had a tensile strength of 211 kg. per sq. cm., and an ultimate elongation of 500 per cent.<sup>233</sup>

The character of the finely divided carbon used modifies the properties of the vulcanized product. It is reported<sup>234</sup> that lampblack produces a more plastic and softer sodium-butadiene rubber with a much lower tensile strength than does carbon-black under the same conditions. It was found that rubber in-

<sup>226</sup> R. Michel, U. S. P. 1,916,629, July 4, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4700. British P. 327,740, 1928; *British Chem. Abs.*, B, 1930, 625.

<sup>227</sup> R. Michel, German P. 516,653, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2845.

<sup>228</sup> French P. 655,217, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 4103. French P. 36,424 addn. to 655,217, 1924; *Chem. Abs.*, 1930, 24, 6065. French P. 37,374, 1929, addn. to 655,217; *Chem. Abs.*, 1931, 25, 2598.

<sup>229</sup> E. Tschunkur and W. Bock, U. S. P. 1,826,846, Oct. 10, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1932, 689. German P. 532,466, 1929.

<sup>230</sup> E. Tschunkur and W. Bock, U. S. P. 1,938,730, Dec. 12, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1574. U. S. P. 1,938,731, Dec. 12, 1933; *Chem. Abs.*, 1934, 28, 1574. K. Meisenburg and W. Bock, U. S. P. 1,938,751, Dec. 12, 1933; *Chem. Abs.*, 1934, 28, 1574.

<sup>231</sup> British P. 334,554, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1931, 78.

<sup>232</sup> British P. 339,255, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1931, 264.

<sup>233</sup> It is reported that a mixture possessing practically the same tensile strength as ordinary synthetic rubber is obtained by using 25 per cent of reclaimed synthetic rubber in the mix and adding pine tar as a softener. See I. Belen'kii, *J. Rubber Ind.* (U. S. S. R.), 1934, 11, 345; *Chem. Abs.*, 1935, 29, 638.

<sup>234</sup> I. Raiz, G. Builo and A. Ermolaev, *J. Rubber Ind.* (U. S. S. R.), 1932, 8, 147; *Chem. Abs.*, 1933, 27, 2337.

creased in hardness very rapidly when the percentage of carbon black was increased above 45 per cent. Since the plasticity of sodium-butadiene rubber renders the ordinary milling operations impossible, methods for reducing such a characteristic are desirable in this instance. Farberov and Merzlikin<sup>286</sup> have reported that beneficial results were observed upon treating the crude synthetic rubber with dry steam in a vulcanizer and subsequently drying the material in a vacuum. A mixture of the resulting product with carbon black showed a decrease in plasticity of 20 per cent, calendered without difficulty and exhibited a 5-10 per cent increase in its resistance to tearing. Bock and Tschunkur<sup>286</sup> have reported that polymerized isoprene or similar hydrocarbons vulcanized in the presence of finely divided carbon black yielded products having an index of strength between 40,000 and 150,000.

Chesnokov<sup>287</sup> found that sodium-butadiene rubber when washed free of metallic sodium vulcanized best.<sup>288</sup> The addition of a naphthenic acid to neutralize the metallic sodium was not advantageous since an additional amount of sulphur was required (about 5.5 per cent more) and, in general, the vulcanization process was retarded. Vulcanization accelerators<sup>288</sup> such as aldehyde ammonia, previously dissolved in a solvent, favor the production of articles having improved elasticity and strength. Water, hydrocarbons, ethers, weak acids and liquid bases may serve as solvents for the accelerators. The addition of a bleached lignite wax to the material to be vulcanized facilitates mechanical treatment such as mixing and kneading.<sup>290</sup> Preservatives, including the hydroxy derivatives of biphenyl<sup>241</sup> and its substitution products and emulsified aldo- $\alpha$ -naphthylamine,<sup>242</sup> are said to be effective in preventing aging. The customary mastication process which precedes vulcanization may be avoided by incorporating the sulphur, fillers and particularly the carbon black while the polymerizate is still in the form of an emulsion.<sup>244</sup> Ermolaev and Bobrova<sup>244</sup> have investigated the effect of various inorganic substances on the properties of finished synthetic rubber products. They found that magnesium oxide was a good reinforcing agent, magnesium carbonate and kaolin produced soft materials indicating a medium reinforcing power, lithopone and zinc oxide have very little reinforcing action, chalk is not effective in this capacity, and barytes and lime can be used only when the product is not required to have elasticity. On the other hand, talc and infusorial earth gave products of excellent elasticity and lightness. Furthermore, Bock and Tschunkur<sup>245</sup> have asserted that such finely divided inorganic compounds can be substituted for lampblack to yield an acceptable synthetic rubber.

<sup>286</sup> M. Farberov and F. Merzlikin, *J. Rubber Ind. (U. S. S. R.)*, 1933, 10, 123; *Chem. Abs.*, 1934, 28, 2944.

<sup>287</sup> W. Bock and E. Tschunkur, U. S. P. 1,911,672, May 30, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4123. French P. 690,043, 1930; *Chem. Abs.*, 1931, 25, 1118. German P. 578,965, 1933; *Chem. Abs.*, 1934, 28, 930.

<sup>288</sup> N. Chesnokov, *J. Rubber Ind. (U. S. S. R.)*, 1933, 9, 34; *Chem. Abs.*, 1933, 27, 5576.

<sup>289</sup> The presence of sodium presents a fire hazard in the calendering operation. See P. Kaplan, *J. Rubber Ind.*, 1934, 11, 139; *Chem. Abs.*, 1934, 28, 7591.

<sup>290</sup> T. Goost, U. S. P. 1,918,466, July 18, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4958. German P. 582,286, 1933; *Chem. Abs.*, 1933, 27, 5218. British P. 335,970, 1929; *Chem. Abs.*, 1931, 25, 2022.

<sup>291</sup> French P. 701,063, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3874. British P. 337,095, 1929; *Chem. Abs.*, 1931, 25, 77.

<sup>292</sup> British P. 550,568, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 770.

<sup>293</sup> H. Tochtermann and C. Heuck, U. S. P. 1,814,420, July 14, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 5811. French P. 682,161, 1929; *Chem. Abs.*, 1930, 24, 4425. German P. 577,731, 1933; *Chem. Abs.*, 1934, 28, 685.

<sup>294</sup> A. Beck and M. Mueller-Cunradi, U. S. P. 1,991,867, Feb. 19, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2396. British P. 368,256, 1930; *Chem. Abs.*, 1933, 27, 2389. French P. 713,354, 1931; *Chem. Abs.*, 1932, 26, 1820. See also French P. 669,943, 1929; *Chem. Abs.*, 1930, 24, 2008.

<sup>295</sup> A. Ermolaev and A. Bobrova, *J. Rubber Ind. (U. S. S. R.)*, 1933, 9, 121; *Chem. Abs.*, 1933, 27, 6019.

<sup>296</sup> W. Bock and E. Tschunkur, German P. 580,540, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1891.

## APPLICATIONS OF POLYMERIZATION PRODUCTS

Interesting possibilities for the industrial utilization of the various polymerization products of olefins and diolefins have been advanced, and suggested applications have been extended to include such fields as the manufacture of automobile tires, electrical insulation, coating compositions, plastics and molded articles, adhesives, and synthetic fibers. The characteristics and uses of synthetic products obtained from chloroprene are dealt with in Chapter 8.

For the manufacture of automobile tires the polymerizates may be used alone or mixed with natural rubber, but in either case the crude material is vulcanized in the presence of lampblack.<sup>246</sup> A method for producing synthetic rubber of a mixed type is described by Tschunkur and Bock.<sup>247</sup> A butadiene polymerization product is mixed with at least 10 per cent by weight of natural rubber, 20-70 per cent of finely divided carbon black based on the weight of the mixture and a vulcanizing agent such as sulphur. Products, as prepared, have a tensile strength of 180 to 250 kg. per sq. cm. at a stretch of 500 to 800 per cent. In general the elasticity of synthetic rubber leaves much to be desired, hence it has been suggested that the treads be made from synthetic rubber and the side walls from natural rubber.<sup>248</sup>

The selection of polymerization products to be used in tire manufacture may be made on the basis of their relative viscosities in solutions of the same concentration.<sup>249</sup> Good resistance to the attrition and wear encountered by the tire treads may be obtained with a polymerizate of high viscosity.<sup>250</sup> For the side walls, however, a material of low viscosity is desirable. A composition for tires is also prepared by mixing butadiene polymerization products with natural or synthetic resins.<sup>251</sup> A mixture recommended for rubber soles for footwear consists of synthetic rubber (25), lampblack (20-30), kaolin (14.5-15), scrap rubber (22-30), sulphur (1.8), zinc oxide (1.5) and calcium oxide (2-3 per cent) and various accelerators and anti-agers.<sup>252</sup>

Since elasticity is not of prime importance in the manufacture of electrical insulating materials, synthetic rubber is readily adaptable to this purpose.<sup>253</sup> Schmidt<sup>254</sup> and his co-workers have prepared insulating products by heating non-distillable polymers of butadiene at 100-500°C. in the presence of a sulphurizing agent until the tensile elasticity is destroyed and the product sufficiently hardened. Insulation for submarine cables has been described<sup>255</sup> comprising 35-40 per cent of deresin-

<sup>246</sup> C. Krauch and M. Mueller-Cunradi, U. S. P. 1,979,946, Nov. 6, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 380. British P. 326,202, 1928, addn. to 299,037, 1928; *Brit. Chem. Abs. B*, 1930, 521. British P. 350,490, 1930; *Brit. Chem. Abs. B*, 1931, 770.

<sup>247</sup> E. Tschunkur and W. Bock, U. S. P. 1,906,667, May 2, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3642. U. S. P. 1,911,729, May 30, 1933, *Chem. Abs.*, 1933, 27, 4133. French P. 699,404, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1119.

<sup>248</sup> C. Krauch and M. Mueller-Cunradi, U. S. P. 1,979,947, Nov. 6, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 380. French P. 37,663, 1929, addn. to 660,634, 1928, *Chem. Abs.*, 1931, 25, 4741.

<sup>249</sup> British P. 240,681, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4744. French P. 699,911, 1930; *Chem. Abs.*, 1931, 25, 3521.

<sup>250</sup> Severe tests made on tires from butadiene rubber have proven them satisfactory. See S. Levin and V. Evratov, *J. Rubber Ind.*, (U. S. S. R.), 1934, 11, 97; *Chem. Abs.*, 1934, 28, 7591.

<sup>251</sup> British P. 324,958, 1929, addn. to 299,037, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1706. French P. 662,603.

<sup>252</sup> A. Pisarenko, *Kozhevenno-Obuvnaya Prom.*, 1934, 13, 619; *Chem. Abs.*, 1935, 29, 2391. Cf. O. Khoikhin and S. Gershikov, *ibid.*, 550; *Chem. Abs.*, 1935, 29, 2391.

<sup>253</sup> See B. Fabritsiev, I. Teikov and A. Suslyakov, *J. Rubber Ind. (U. S. S. R.)*, 1934, 11, 223; *Chem. Abs.*, 1935, 29, 638.

<sup>254</sup> O. Schmidt, G. Niemann and E. Meyer, U. S. P. 1,832,976, Oct. 18, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 862. O. Schmidt, B. Schnell and E. Meyer, U. S. P. 1,901,044, Mar. 14, 1933; *Chem. Abs.*, 1933, 27, 3018. German P. 518,328, 1929; *Chem. Abs.*, 1931, 25, 2408. French P. 694,151, 1930; *Chem. Abs.*, 1931, 25, 1926.

<sup>255</sup> British P. 369,647, 1930, to Felten & Guillaume Carlswerke A.-G.; *Brit. Chem. Abs. B*, 1932, 646. German P. 558,245, 1930; *Chem. Abs.*, 1933, 27, 862. Cf. British P. 379,941, 1932; *Chem. Abs.*, 1933, 27, 3543.

ized gutta-percha or balata, 35-45 per cent of synthetic rubber and 10-30 per cent of hydrogenated synthetic or natural dealbuminized rubber. Submarine cables, designed to prevent incorporated magnetic material from being subjected to strains due to pressure and bending,<sup>254</sup> are filled with a polymerized cyclic terpene hydrocarbon as a pressure-equalizing compound. Rubber, gutta-percha or balata may be used along with the polymer. Cables may be coated also with a polymerization product of butadiene to which has been added magnesium oxide, lampblack and sulphur along with accelerators and anti-aging substances. The insulation is vulcanized at 100-150°C.<sup>257</sup>

Rubber dielectric compositions have been prepared in which a synthetic hydrocarbon polymerization product, e.g., polymerized styrene or butadiene, may comprise as much as 80 per cent of the composition, the remaining 20 per cent being rubber, gutta-percha or balata or a mixture of these.<sup>255</sup> A somewhat novel procedure involves the mibbing of the styrene by the rubber after which the styrene is polymerized by heating at 100° for 7-14 days. The composition is obtained in its finished form by masticating the polymerization mixture with wax.

Since synthetic rubber-like products may be obtained in a plastic condition, they may be molded or shaped and vulcanized until quite hard, thus yielding useful articles of many kinds. For example, Tschunkur and Bock<sup>256</sup> describe frost-resisting vessels which do not harden or become brittle at low temperatures. The plastic material comprises a mixture of polymerized isoprene and dimethylbutadiene mixed with sulphur, zinc oxide, tar, stearic acid, lampblack and diphenylguanidine. Hard masses for the manufacture of molded articles<sup>260</sup> are obtained by heating, without sulphur, the non-distillable polymers of butadiene or its derivatives to 100-500°C. However, before heating there may be added other polymerization products, solvents, rubber, fillers, coloring matter and plasticizers. The resulting resin may be similar to ebonite with good electrical insulating properties or it may be soft and pliable, depending upon the conditions of the reaction and added materials. Other similar hardened products have also been described.<sup>261</sup> A hard rubber-like composition said to be resistant to heat and chemical reagents has been prepared by Zieser<sup>262</sup> who polymerized mixtures of butadiene, natural rubber and sulphur using an alkali metal as the catalyst. The proportions of rubber used varied between 40 and 80 per cent and the proportion of sulphur added was large.

Synthetic rubber, such as may be obtained from isoprene, butadiene or dimethylbutadiene, is used in conjunction with other natural or synthetic plastic substances in the manufacture of products resembling leather, linoleum, ebonite, celluloid and artificial wood.<sup>263</sup> For example, a linoleum substitute contains 8 parts of dimethylbutadiene rubber, 5 parts of rosin, 5 parts of a mineral oil, 50 parts of cork, sawdust, peat meal, cellulose acetate or the like, 10 parts of heavy spar or lithopone, 12 parts of magnesia and 10 parts of ochre. After thorough mixing, the plastic

<sup>254</sup> A. R. Kemp, U. S. P. 1,892,279, Dec. 27, 1932, to Bell Telephone Laboratories, Inc.; *Chem. Abs.*, 1933, 27, 1833. British P. 378,502, 1932, to Electrical Research Products, Inc.; *Chem. Abs.*, 1933, 27, 3641. U. S. P. 1,882,031, 1932; *Brit. Chem. Abs.* B, 1933, 717. British P. 404,027, 1934, *Chem. Abs.*, 1934, 28, 3939.

<sup>255</sup> British P. 332,891, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 549.

<sup>256</sup> M. C. Field, W. E. Hugh and L. G. B. Parsons, British P. 357,624, 1930, to Standard Telephones & Cables, Ltd.; *Chem. Abs.*, 1933, 27, 443.

<sup>257</sup> E. Tschunkur and W. Bock, German P. 551,967, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4982.

<sup>258</sup> British P. 323,012, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2917. French P. 674,679, 1929; *Chem. Abs.*, 1930, 24, 2816. See also British P. 304,612, 1929, *Brit. Chem. Abs.* B, 1930, 677. British P. 345,239, 1929; *Brit. Chem. Abs.*, B, 1931, 599. O. Schmidt and E. Meyer, German P. 557,751, 1928; *Chem. Abs.*, 1932, 26, 4982.

<sup>259</sup> French P. 690,484, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1119. French P. 691,357, 1929; *Chem. Abs.*, 1931, 25, 1119. French P. 692,606, 1930; *Chem. Abs.*, 1931, 25, 1706. French P. 715,704, 1931; *Chem. Abs.*, 1932, 26, 1620. British P. 332,557, 1929; *Brit. Chem. Abs.* B, 1930, 981.

<sup>260</sup> W. Zieser, U. S. P. 1,932,390, Oct. 31, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 678.

<sup>261</sup> British P. 304,612, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 677. French P. 667,409, 1929; *Chem. Abs.*, 1930, 24, 1189. German P. 575,236, 1933; *Chem. Abs.*, 1933, 27, 3581.

mass is rolled into sheets. A similar preparation<sup>264</sup> contains along with the usual fillers, methyl rubber W, nitrocellulose or linoxyn.

Coating compositions of various kinds have been described in which synthetic rubber products are the essential ingredients. Synthetic rubber in colloidal dispersions has been suggested as a base for the preparation of varnishes and lacquers.<sup>265</sup> A varnish-like material for coating the textile covering of airplane wings<sup>266</sup> contains polymerized butadiene hydrocarbons. Quick-drying coating materials<sup>267</sup> said to be transparent to light in a layer 2 inches in thickness are prepared by fractionating vapor-phase-cracked gasoline and polymerizing a fraction with a maximum boiling point of 112°C. Lacquer coatings<sup>268</sup> have been prepared from polymerization products hardened by air or oxygen in the presence of catalysts or by treatment with aluminum chloride, sulphur or sulphur dichloride. Complex products said to be useful as lacquer components may be derived from the polymerization of mixtures of butadiene and stand oil (linseed oil previously heated to 315°C. without driers).<sup>269</sup> Squalene, a hydrocarbon of the formula  $C_{40}H_{70}$  containing 6 conjugated double bonds and 8 methyl groups, was found to be of little value in paint making, since films of its polymerization product were quite brittle, swelled in water and were completely destroyed by sodium hydroxide.<sup>270</sup>

A road-making composition recommended by Bond<sup>271</sup> is prepared by stabilizing an aqueous dispersion of synthetic rubber through the addition of at least 150 per cent by weight of portland cement. Vulcanizing agents and compounding ingredients may also be included to suit the particular conditions under which the material is to be used. It is also said that the addition of 1-20 per cent of diolefin polymerizates produces a beneficial effect upon the elasticity and stability of road-construction materials when subjected to cold weather.<sup>272</sup> Brown<sup>273</sup> advocates employing synthetic rubber as a coating for a plastic, bituminous flooring material.

A somewhat unusual application of polymerization products has been proposed in the preparation of a substitute for reinforced glass.<sup>274</sup> The method of manufacture involves the application of a soft coating of a polymerization product of butadiene to an open-meshed fabric such as a mesh of tinned iron wire or vegetable fiber and hardening the film with oxygen or heat. A hard, transparent product results. Hydrogenated butadiene polymers are said to be applicable as an intermediate layer between two glass sheets in the manufacture of non-splintering glass.<sup>275</sup>

The polymerization products of butadiene and other diolefins along with their condensation and transformation products have been found adaptable to the manufacture of synthetic fibers, foils and the like. A characteristic process for the preparation of foils and threads<sup>276</sup> consists in coating glass plates with synthetic rubber (from butadiene) dissolved in cyclohexane or methylene dichloride. After

<sup>264</sup> British P. 348,077, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 449. See also British P. 399,856, 1933, to Behr-Manning Corp.; *Chem. Abs.*, 1934, 28, 1823.

<sup>265</sup> French P. 717,087, 1931, to Radiochemisches Forschungs-Institute G. m b H.; *Chem. Abs.*, 1932, 26, 2879.

<sup>266</sup> German P. 512,526, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1393.

<sup>267</sup> J. Hyman, U. S. P. 1,919,722; 1,919,723, July 25, 1933, to Velsicol Corp.; *Chem. Abs.*, 1933, 27, 4942.

<sup>268</sup> British P. 334,961, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1412. French P. 687,773, 1930; *Chem. Abs.*, 1931, 25, 785.

<sup>269</sup> O. Jordan, H. Hopff and E. Kühn, German P. 588,306, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1558.

<sup>270</sup> P. Slansky, *Fettchem. Umschau* 1933, 40, 77; *Chem. Abs.*, 1933, 27, 3091.

<sup>271</sup> A. E. Bond, British P. 369,561, 1930, to R. Cntohley, Ltd.; *Brit. Chem. Abs. B*, 1932, 651.

<sup>272</sup> British P. 337,521, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 160.

<sup>273</sup> R. Brown, British P. 372,081, 1931, addn to 342,398; *Chem. Abs.*, 1933, 27, 3318.

<sup>274</sup> O. Schmidt, German P. 536,119, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1087. British P. 336,075, 1929; *Chem. Abs.*, 1931, 25, 2022. French P. 734,688, 1932; *Chem. Abs.*, 1933, 27, 1128. French P. 699,514, 1930; *Chem. Abs.*, 1931, 25, 3449.

<sup>275</sup> M. Dunkel, W. Breuers and W. Wolf, German P. 593,465, 1934; *Chem. Abs.*, 1934, 28, 3203.

<sup>276</sup> British P. 327,164, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5182. French P. 27,485, 1929, addn. to 676,658, 1929; *Chem. Abs.*, 1931, 25, 2597. See also O. Schmidt, German P. 568,906, 1928; *Chem. Abs.*, 1933, 27, 2845. German P. 533,145, 1933; *Chem. Abs.*, 1934, 28, 1222. German P. 377,732, 1933; *Chem. Abs.*, 1934, 28, 685.

the solvent has evaporated the product is treated with sulphur chloride vapor to form a thin transparent foil. Threads are made in a similar manner except that the rubber solution is forced through an orifice to form the filament. A crimped or curled effect can be imparted to the fiber<sup>277</sup> by immersion in organic swelling agents such as solutions or emulsions of dipentene, cyclohexane, ethers, esters, and ketones. For example, a fiber with a wool-like appearance results by allowing dipentene to exert its action upon the threads for 100 minutes at 45°C.

Wulff, Moll and Breuers<sup>278</sup> state that the addition of about 0.5 per cent of hydrocarbons such as polymerized styrene, indene and hydrogenated natural or synthetic rubber greatly improves the viscosity, pour point and stability of lubricating oils. Alternatively the unpolymerized hydrocarbons may be added and subsequently polymerized *in situ*.

Other uses for diene polymerization products include the utilization of their benzene solutions as adhesives.<sup>279</sup> Thus, solutions of mixtures resulting from the polymerization of butadiene or isoprene with balata, gutta-percha or rubber are recommended for bonding rubber to metals.<sup>280</sup> Synthetic rubber coating compositions may also be used in conjunction with water-sensitive adhesives in the preparation of stamps to be used on regenerated cellulose surfaces.<sup>281</sup> High polymers of isobutylene have been suggested as adhesives for safety glass, plywood and adhesive plasters.<sup>282</sup> Also, similar polymerization products when incorporated with kieselguhr and vulcanized in the presence of sulphur, zinc oxide, diphenylguanidine and naphthylamine, yield porous sheets for use in electrolytic cells.<sup>283</sup> Another preparation recommends the addition of rosin-ethylene oxide resins.<sup>284</sup>

Schmidt and Bock<sup>285</sup> have made use of polymerization products in the manufacture of colloidal solutions and pastes of insoluble dyes and pigments. The polymerizates, prepared in the usual way, are ground with the other components and the colloidal solution is formed by the subsequent addition of an organic solvent.

In order to impart additional rubber-like qualities to polymerized isoprene, Pratt<sup>286</sup> dispersed the material in water and coated the colloidal particles with albumin or casein. By adding a tanning agent the strength and toughness of the protein coating is increased.

<sup>277</sup> French P. 693,921, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2008. French P. 692,027, 1930; *Chem. Abs.*, 1931, 25, 1392. British P. 346,799, 1929; *Chem. Abs.*, 1932, 26, 2067.

<sup>278</sup> C. Wulff, F. Moll and W. Breuers, German P. 557,306, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 410. British P. 399,527, 1932. *Brit. Chem. Abs.* B, 1933, 997. British P. 379,717, 1931; *Brit. Chem. Abs.*, B, 1932, 971. See also French P. 758,269, 1934; *Chem. Abs.*, 1934, 28, 3230. See also British P. 411,893, 1932; *Brit. Chem. Abs.* B, 1934, 749. French P. 758,269, 1934, *Chem. Abs.*, 1934, 28, 3230.

<sup>279</sup> French P. 685,745, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5951. German P. 545,861, 1928, *Chem. Abs.*, 1932, 26, 3633. German P. 526,106, 1928; *Chem. Abs.*, 1931, 25, 4373.

<sup>280</sup> D. F. Twiss, F. A. Jones and J. H. Anderson, U. S. P. 1,931,879, Oct. 24, 1933, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1934, 28, 687. British P. 398,430, 1933; *Chem. Abs.*, 1934, 28, 687.

<sup>281</sup> E. B. Bengier, U. S. P. 1,953,946, Apr. 10, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3850.

<sup>282</sup> French P. 775,306, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2625.

<sup>283</sup> British P. 331,197, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 39. French P. 668,045, 1929; *Chem. Abs.*, 1930, 24, 1545.

<sup>284</sup> British P. 331,227, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 830. Cf. French P. 667,957, 1929; *Chem. Zentr.*, 1930, 2, 1455. See also Chapter 38.

<sup>285</sup> O. Schmidt and B. von Bock, German P. 549,205, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3886. French P. 689,711, 1930; *Chem. Abs.*, 1931, 25, 1046.

<sup>286</sup> W. B. Pratt, U. S. P. 1,671,314, May 29, 1928, to Dispersions Process, Inc.; *Chem. Abs.*, 1928, 22,



## Chapter 10

### Resins from Petroleum

The possibility of employing petroleum as a cheap and abundant material for the production of resins has attracted considerable attention. Although it must be admitted that many of such products thus far obtained from petroleum are of an inferior grade, being dark in color and either soft or very brittle, at least one type, namely, that obtained by the polymerization of highly cracked gasoline, appears to have commercial significance.

Both neutral and acidic resinous bodies are present in natural petroleum though generally in relatively small proportions. Such substances are not strictly synthetic in the usually accepted sense of the word. They are discussed in this chapter, however, because of their possible utilization. Resins have been produced also by the condensation of petroleum distillates and residuums. Artificial asphalts belong to the class of oxidized petroleum and are only briefly mentioned since they are more fully discussed in other treatises. The conversion of petroleum hydrocarbons into resins by condensation with various reagents, e.g., formaldehyde, acids, or sulphur, has been suggested from time to time but apparently little progress has been made in this direction.

Cracking, or thermal decomposition, of petroleum distillates under proper conditions yields unsaturated hydrocarbons, monolefins and diolefins, which can be polymerized to resinous materials. Methods for the preparation of the latter are discussed in Chapter 9. Cracking petroleum hydrocarbons (for example, methane or natural gas) at very high temperatures gives resin-forming hydrocarbons including butadiene and, probably, also indene.

Oxidation of cracked hydrocarbon mixtures, such as cracked gasoline, proceeds spontaneously with the formation of resinous or gummy bodies. Treatment with refining agents (sulphuric acid, activated absorbent earths or zinc chloride) also converts unsaturated hydrocarbons of this type into resins. Since the latter substances are by-products of a large industry and could be available in great quantity, the separation of high-grade products, therefore, offers commercial possibilities. So far, however, little success apparently has attended efforts to utilize these by-products of refining.

#### RESINS OF PETROLEUM

The resinous and asphaltic constituents of petroleum consist of two classes, hydrocarbons and oxygenated compounds of high molecular weight.<sup>1</sup> The latter are composed of acidic bodies, neutral resins and asphaltic materials. Asphaltenes and carbenes often contain relatively large proportions of combined sulphur. Nevertheless, it is possible that neither sulphur nor oxygen is an essential constituent of such materials since an asphaltene of the formula  $C_{60}H_{100}$  and sp.gr. 1.023 has been isolated.

<sup>1</sup> D. Holde and R. Eickmann, *Petroleum*, 1907, 2, 1077; *Chem. Abs.*, 1908, 2, 1341. *Mitt. kgl. Materialprüfungsamt.*, 25, 8; *Chem. Abs.*, 1908, 2, 177.

The various types of resinous matter are differentiated by their solubility in organic solvents. Petroleum resins, which resemble vegetable resins in some of their properties, are extracted from distillates with 70 per cent alcohol.<sup>2</sup> Other extraction solvents which may be employed, particularly with lubricating or turbine oils, are acetone or castor oil<sup>3</sup> and a mixture of methyl alcohol and a hydroaromatic hydrocarbon such as cyclohexane.<sup>4</sup> These resins are described as oxygen- and sulphur-containing, terpene-like hydrocarbons. A more convenient method consists in treating the distillate with an absorption agent, e.g., animal charcoal or Florida earth. The latter is then extracted with benzene (to remove oil) and afterwards successively with ether, benzene and chloroform.<sup>5</sup> This procedure results in a partial fractionation of the resins, as indicated by a gradual increase in the specific gravity, viscosity and oxygen and sulphur contents, and decrease in proportions of carbon and hydrogen, of the extracted products.

According to Borodulin<sup>6</sup> the resinous constituents of petroleum distillates are (a) asphaltenes or (b) unsaturated hydrocarbons which are easily converted to resins, e.g., by polymerization or oxidation. The former are precipitated by the addition of petroleum ether<sup>7</sup> or are removed by Floridin or animal charcoal. Unsaturated hydrocarbons are resinated by treatment of the distillate with alcoholic sodium hydroxide,<sup>8</sup> sulphuric acid or formaldehyde (see discussion of formolites on pages 211-214).

Benzene, or petroleum ether, employed in the quantitative precipitation of asphaltenes should correspond to the following specifications:<sup>9</sup>  $d_{15}^{20}$  0.695-0.705, a boiling range of 65-95°C., and not more than 2 per cent be soluble in a mixture of 80 parts of 96 per cent sulphuric acid and 20 parts of fuming acid (20 per cent  $\text{SO}_3$ ). Other suggested precipitants are acetone,<sup>10</sup> ethyl acetate<sup>11</sup> and methyl ethyl ketone saturated with water.<sup>12</sup>

Carbenes and carboids are types of substances representing successive decomposition (or possibly condensation) products of asphaltenes.<sup>13</sup> Both possess a lustrous black color and resemble coal in appearance. Carbenes are insoluble in cold carbon tetrachloride and carboids in all organic solvents.

**Neutral Resins.** Neutral resins, asphaltenes, carbenes, and carboids form a series of oxygenated substances of increasing molecular complexity and diminishing solubility. Marcusson<sup>14</sup> considers petroleum resins are the first stage in the conversion of high-molecular-weight petroleum hydrocarbons into asphaltenes and describes them as being soluble in petroleum spirit, chloroform, carbon disulphide and benzol and having a specific gravity of about 1. Nitration indicates that both resins and asphalt are apparently polycyclic compounds. At 100°C. sulphuric acid changes these resins into insoluble sulphur compounds. Sulphuric acid and

<sup>2</sup> D. Holde and R. Eickmann, *loc. cit.*

<sup>3</sup> F. Schwartz and J. Marcusson, *Z. angew. Chem.*, 1913, 26, 385; *Chem. Abs.*, 1913, 7, 3019

<sup>4</sup> C. Krauch, M. Pier and A. Eisenhut, U. S. P. 1,960,974, May 29, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 4587.

<sup>5</sup> D. Holde and R. Eickmann, *loc. cit.* See also P. Smirnov, *Neft Khoz.*, 1925, 8, 286; *J.S.C.I.*, 1925, 44, 836B.

<sup>6</sup> M. W. Borodulin, *Petroleum Z.*, 1927, 23, 1515

<sup>7</sup> V. E. Rakovski and S. I. Rubin (*Khim. Tverd. Topl.*, 1934, 5, 131; *Chem. Abs.*, 1934, 28, 6282) suggest petroleum ether as a precipitant for asphaltenes, paraffin and other solids from low-temperature tar.

<sup>8</sup> R. Kissling, *Chem.-Ztg.*, 1907, 31, 328; *J.S.C.I.*, 1907, 26, 463; *Chem.-Ztg.*, 1908, 32, 938; *J.S.C.I.*, 1908, 27, 1053. K. Weissberg, *Petroleum Z.*, 1934, 30 (4), 5; *Brit. Chem. Abs.*, B, 1934, 308.

<sup>9</sup> D. Holde and R. Eickmann, *loc. cit.* D. Holde, *Chem.-Ztg.*, 1914, 38, 241. See also H. Burstin and J. Winkler, *Przemysl Chem.*, 1928, 12, 445; *Chem. Abs.*, 1928, 22, 4786. *Erdol u. Teer*, 1926, 5, 26, 42, 62; *Chem. Abs.*, 1929, 23, 2289.

<sup>10</sup> F. Schwartz and H. Schluter, *Chem.-Ztg.*, 1911, 35, 413

<sup>11</sup> H. Kantorowicz, *Chem.-Ztg.*, 1913, 37, 1438. The use of this liquid is contested by D. Holde and G. Meyerheim (*Chem.-Ztg.*, 1914, 38, 241, 264)

<sup>12</sup> F. Schwartz, *Chem.-Ztg.*, 1911, 35, 1417

<sup>13</sup> J. Marcusson, *Chem.-Ztg.*, 1913, 42, 437; *J.S.C.I.*, 1919, 38, 98A

<sup>14</sup> J. Marcusson, *Z. angew. Chem.*, 1916, 29, 346; *J.S.C.I.*, 1916, 35, 1099. *Chem.-Ztg.*, 1915, 39, 581, 613.

formaldehyde react with the resins to form sparingly soluble precipitates. When heated for some time at 120°C. neutral resins become insoluble in petroleum ether, deep black in color and are transformed into asphaltenes.

Resinous components of lubricating oils are present to the extent of a few tenths of a per cent and can be separated from the hydrocarbons with alcohol and ether.<sup>15</sup> They are solid, oxygenated, lac-like bodies and may be a cause of gumming as their removal appears to decrease the gumming tendency of lubricants.

Neutral resins can be separated from oils and oxygenated materials by the following method.<sup>16</sup> The oil is washed with caustic soda solution to remove naphthenic and asphaltogenic acids. Asphaltenes are precipitated by the addition of petroleum ether and the residual oil is treated at 50°C. with silica gel in amounts determined by the resin content.<sup>17</sup> Fuller's earth is not as satisfactory as it adsorbs only 20 per cent as much resin and also effects polymerization. Adsorbed oil is removed from the gel with benzene and the resins are extracted with chloroform or a mixture of benzene and ethyl alcohol. The products obtained in this manner are neutral and only slightly unsaturated. Their molecular weights (in benzene) vary from 226 to 1112 and they form a series of oxygenated compounds of the formula<sup>18</sup>  $C_nH_{2n-m}O_p$ , in which  $n$  varies from 16 to 69,  $m$  from 8 to 48, and  $p$  from 1 to 3. Although unstable, these resins can be distilled at low pressure and give no evidence of colloidal behavior. However, they are easily transformed into asphaltenes by oxidation, which is accompanied by loss of hydrogen and further condensation. Sulphuric acid reacts with them to form asphaltenes and also sulphonates. Both neutral resins and asphaltenes are attacked by perbenzoic acid but not by iodine.<sup>19</sup>

An examination of the resins formed during the distillation of petroleum was made by Siebenek<sup>20</sup> who reported that these substances distilled over with steam at 400°C. in a yield of about 0.3 per cent. The crude materials had specific gravities greater than 1, softening points about 45° and flow points about 60°. Purification was accomplished by drying at ordinary pressure. Though not completely soluble in benzene, the dried resins were wholly soluble in benzene and analogous coal-tar distillates. By vacuum and steam distillation the crude material was separated into an oil (17 per cent of the total) and several resin fractions as follows:

Resin 1 (11 per cent).

Resin 2 (29 per cent), softening at 53°C. and flowing at 70°C.

Resin 3 (13 per cent), softening at 55°C. and flowing at 72°C.

Resins 2 and 3, constituting 42 per cent of the crude, were dark yellow in color and stated to be valuable technically.

Tweddle<sup>21</sup> suggests treating an orange-colored, resinous, oily residue from the distillation of crude petroleum with benzene, thereby obtaining a yellow crystalline precipitate which is termed petrocene. This substance (sp.gr. 1.204) melts at 420-430°C., but if heated to higher temperatures it sublimes and distils, giving off brilliant yellow fumes. Its spectrum is somewhat similar to that for anthracene, possibly indicating petrocene to be a polycyclic hydrocarbon. By appropriate treatment it may be transformed into dyes and other coloring materials.

<sup>15</sup> A. E. Dunstan and F. B. Thole, *Chem. Met. Eng.*, 1923, 28, 299. A. Seton, *J.S.C.I.*, 1929, 48, 81; *Chem. Abs.*, 1929, 23, 2026.

<sup>16</sup> A. Sachanen and N. A. Vasiliev, *Petroleum Z.*, 1927, 23, 1618; *Brit. Chem. Abs.* B, 1928, 78. See also N. A. Vasiliev and L. N. Zhirnova, *Neft. Khoz.*, 1929, 17, 707; *Chem. Abs.*, 1930, 24, 2869.

<sup>17</sup> V. Tokmunov (*Neft. Khoz.*, 1927, 12, 414, 558; 1928, 15, 73; *Chem. Abs.*, 1928, 22, 4786; 1929, 23, 2026) proposed a method of separating mazout and ozocerite into neutral tars and soft asphalt (adsorbed by silica gel), unsaturated compounds and aromatics (adsorbed by activated silica gel) and paraffins and naphthenes (unadsorbed).

<sup>18</sup> The sulphur content corresponds to less than 1 atom and is therefore calculated with the oxygen.

<sup>19</sup> S. S. Nametkin and V. G. Putzello, *Neft. Khoz.*, 1929, 16, 230; *Brit. Chem. Abs.* B, 1930, 130.

<sup>20</sup> H. Siebenek, *Petroleum Z.*, 1923, 19, 939; *Chem. Abs.*, 1924, 18, 462.

<sup>21</sup> H. C. W. Tweddle, U. S. P. 189,402, Apr. 10, 1877.

Resins are prepared from heavy residual hydrocarbons, of petroliferous origin, by submitting the latter to distillation at low pressures (to remove oily constituents) and extracting with a hydrocarbon solvent, e.g., kerosene or naphtha.<sup>22</sup> The last operation precipitates asphaltenes. Aqueous emulsions of such oil-soluble resins are proposed as sizing agents for paper, for impregnation of porous paper and in the manufacture of laminated paper and board.<sup>23</sup>

Incorporation of tar pitch and picoline with petroleum residues, by the application of heat, to give synthetic resins is described by Maslyanskii.<sup>24</sup>

**Asphaltenes.** These are present in crude petroleum, particularly in the higher-boiling fractions and residuums from distillation. They are formed probably from the aromatic constituents of an oil by condensation and polymerization, asphaltic resins being an intermediate stage. Asphaltenes having the following composition, carbon 71.6 per cent, hydrogen 6.3 per cent, oxygen 13.3 per cent and sulphur 8.1 per cent, were prepared by heating naphthenes or paraffins with sulphur and then oxidizing with air.<sup>25</sup> The so-called asphaltenes obtained from acid sludge differ from normal asphaltenes in being soluble in basic solvents. They are coagulated by heating to 100°C. and are probably oxonium compounds derived from sulphuric acid.

Asphaltenes are brown to black in color, have no apparent melting point and decompose to gas and coke at 300°C. They are insoluble in petroleum ether, alcohol, water and most other solvents but dissolve in carbon tetrachloride. Solution is preceded by swelling of the material and results in the formation of a viscous liquid. The latter appears to be colloidal and highly dispersed and as stable as aqueous gelatin solutions. Asphaltenes are lyophile colloids with respect to aromatic hydrocarbons, halogenated hydrocarbons, carbon disulphide and petroleum tars and are lyophobic with respect to paraffin hydrocarbons and naphthenes.<sup>26</sup> Their molecular weights are about 5000-6000 and they contain appreciable proportions of oxygen and usually some combined sulphur. Substances of this type precipitated from Grozny petroleum contained 85.5 per cent carbon, 6.8 per cent hydrogen, 7.7 per cent oxygen and some sulphur and had a density of 1.145.

Oxidation of the higher fractions of petroleum with air or oxygen at elevated temperatures yields asphaltenes. The work of Chernozhukov,<sup>27</sup> however, indicates that the presence of sulphur compounds is essential during oxidation. Thus, oxidation of liquid paraffin, free of sulphur, by oxygen at 250°C. and 12 atmospheres pressure for 2 hours gave a yellow oil from which a flaky sediment could be precipitated, but no asphaltenes or carbenes were formed. Similar treatment of sulphur-free oils to which sulphur was added yielded synthetic asphaltenes possessing the properties of natural asphaltenes but of lower molecular weights. Various asphaltenes were prepared by oxidation of sulphur-containing crude oils with air or oxygen under pressure. Those from a turbine oil distillate had the empirical formula  $C_{172}H_{176}O_{11}S$ , and those from a light spindle oil the formula  $C_{136}H_{140}O_{12}S$ . Chernozhukov concluded that sulphur compounds of unknown constitution and of various stages of oxidation are responsible for the production of asphaltenes. The important role of sulphur compounds in this respect is indicated also by the observation that resinous deposits, obtained from Boryslaw (Galicia)

<sup>22</sup> French P. 744,169, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 4109.

<sup>23</sup> Carleton Ellis, U. S. P. 1,948,442, Feb. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, 28, 2906.

<sup>24</sup> N. A. Maslyanskii, Russian P. 23,268, 1930; *Chem. Abs.*, 1933, 27, 3837.

<sup>25</sup> V. Kalichevsky and S. C. Fulton, *Nat. Pet. News*, 1931, 23 (51), 33.

<sup>26</sup> A. Sachanen, *Neft. Khoz.*, 1924, 7, 933; *Chem. Zentr.*, 1925, 1, 1828. *Petroleum Z.*, 1925, 31, 1441; *J.S.C.I.*, 1925, 44, 745.

<sup>27</sup> A. I. Chernozhukov, *Neft. Khoz.*, 1928, 15, 670; *Chem. Abs.*, 1929, 23, 1258. *Soyuzneft-Neftyanoe Izdatelstvo Moscow-Petrograd*, 1930, 36; *Chem. Abs.*, 1931, 25, 5757.

paraffin oils on storage, had a sulphur content of 2.5 per cent whereas the crude oil contained only 0.1 per cent sulphur.<sup>28</sup>

Elimination of asphaltenes and other dark-colored substances from natural or artificial asphalts furnishes lighter-colored products which may be employed in the manufacture of asphalt paper, lacquers, varnishes or paints.<sup>29</sup> Purification consists in the addition of a precipitant, such as aromatic-free gasoline or pentane, to the molten crude material. Further treatment of the asphalt solution with decolorizing agents, e.g., bleaching earths, is also advantageous. A combination of physical and chemical methods may be used. For example, after dilution with the precipitant the solution of asphalt is subjected to the action of sulphuric acid, anhydrous aluminum chloride, ferric chloride or boron fluoride. The latter procedure converts any dissolved asphaltenes into insoluble substances.

Resinous or asphaltic materials are precipitated from mineral oils by warm, dilute sulphuric acid (1-10 per cent soln.)<sup>30</sup> or by allowing the oil to stand in contact with concentrated aqueous solutions of heavy metal salts, especially the chlorides.<sup>31</sup>

Moderate hydrogenation of asphaltenes, particularly in the presence of a hydrocarbon solvent, transforms them into resins or resin-like bodies.<sup>32</sup>

Discussion of more complex oxygenated materials, including carbenes, carboids and asphalts, are beyond the scope of this text. Resins made by oxidation of various petroleum fractions are described later.

**Petroleum Acids.** Carboxylic acids in petroleum, which are comprehended under the generic name of naphthenic acids, are of technical and scientific interest.<sup>33</sup> These acids differ considerably in physical properties, depending upon their origin. Those of low molecular weight are volatile oils of penetrating odor and consist mainly of monocarboxylic acids containing one cyclopentane ring. Bicyclic and possibly other polycyclic monocarboxylic acids are present also in Rumanian, German, Californian and Texas crudes.<sup>34</sup> High molecular weight acids, such as those from lubricating stocks, are viscous liquids and, in some instances, semi-solid materials.

Acids isolated from certain lubricating oils of American origin are of special interest.<sup>35</sup> These are monocarboxylic acids of the series  $C_nH_{2n-6}O_2$  and  $C_nH_{2n-8}O_2$  ( $n$  varying from 16 to 25) having molecular weights ranging from 250 to 376. They are viscous liquids which do not solidify at  $-30^\circ C.$ , are non-volatile in steam and do not absorb oxygen or "dry" on exposure to air. Salts of these acids are soluble in gasoline, ether and carbon tetrachloride while the lithium, ammonium, potassium, sodium and magnesium salts are soluble in water. The acids are prepared in the following manner.

Gasoline vapors are passed into alkali sludge obtained by washing acid-treated

<sup>28</sup> S. von Pilat and J. Dukiet, *Erdöl u. Teer*, 1926, 2, 571, *Chem. Abs.*, 1926, 20, 3560.

<sup>29</sup> J. W. leNobel, U. S. P. 1,868,211, July 19, 1932, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1932, 26, 5220. British P. 313,433, 1928; *Brit. Chem. Abs. B*, 1930, 93.

<sup>30</sup> R. N. Donaldson and R. McCollum, U. S. P. 1,508,115, Aug. 26, 1924, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1924, 18, 3270.

<sup>31</sup> French P. 670,796, 1929, to N. V. Mejnbouw- en Cultuurmaatschappij "Boeton"; *Chem. Abs.*, 1930, 24, 1970.

<sup>32</sup> French P. 744,220, 1933, to International Hydrogenation Patents Co., Ltd.; *Chem. Abs.*, 1933, 27, 4109.

<sup>33</sup> Asphaltic acids and asphaltic anhydrides are described by V. Kalchevsky and S. C. Fulton (*loc. cit.*) but little is known about them. They are sparingly soluble in light naphtha, have relatively high specific gravities and are unstable. They are readily distinguished from true naphthenic acids which are stable and saturated in character. See also J. Marcusson, *Z. angew. Chem.*, 1918, 29, 346, *J.S.C.I.*, 1918, 35, 1099.

<sup>34</sup> J. von Braun, *Ann.*, 1931, 490, 100. For a summary of the physical and chemical properties of naphthenic acids occurring in petroleum, see, Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

<sup>35</sup> G. Alleman, U. S. P. 1,694,461, 1,694,462 and 1,694,463, Dec. 11, 1928, to Sun Oil Co.; *Chem. Abs.*, 1929, 23, 696. See also H. T. Matland, U. S. P. 1,425,887, 1,425,883, 1,425,884 and 1,425,885, Aug. 15, 1922, and 1,528,884, Mar. 10, 1925 to Sun Oil Co.; *Chem. Abs.* 1922, 16, 3388; 1925, 19, 1502.

lubricating distillates. This results in a separation into oil and water layers and is facilitated by the addition of 0.1 per cent by volume (on the sludge) of a saturated solution of sodium chloride. Dissolved resins are removed by the gasoline-oil layer. The oil-free soap solution (water layer) is concentrated and then cooled to  $-5^{\circ}\text{C}.$  at which temperature precipitation of soap occurs. This may be hastened by cooling to slightly lower temperatures. The soap is decomposed by acidification or by hydrolysis with steam under pressure and the free acids further purified by distillation under reduced pressure. Acids obtained directly from the soap have an acid number of about 103. The acid number of the distilled product is usually greater. For example, distillation of the acids under 4 mm. pressure yielded the following fractions:

Fraction	Temperature	Acid No.
1 . .	Up to $180^{\circ}\text{C}.$	187
2	$180\text{--}190^{\circ}\text{C}.$	174
3 .	$190\text{--}200^{\circ}\text{C}.$	160
Residue	Acid + Resins	61

Another method of purification consists in acidifying the aqueous solution of alkali salts, adding xylene, and removing water by distillation of the mixture.<sup>85a</sup> The residue is separated into acids and insoluble colloidal hydrocarbons by extraction with ethyl alcohol.

In the preparation of metallic derivatives either the purified soap or acids derived therefrom, without preliminary distillation, may be used. Thus, addition of a solution of calcium chloride to an aqueous solution of the soap gives the calcium salt which is a light-colored, sticky, tenacious mass practically insoluble in water and can be washed free of entrained salts by agitation with water.<sup>86</sup> It is slightly soluble in methyl or ethyl alcohol and acetone, very soluble in ethyl acetate, carbon tetrachloride, gasoline, benzene or ether and dissolves to some extent in turpentine and linseed oil. The calcium salt may be used in numerous ways, for example, as a water-proofing material, adhesive, wood filler, grafting wax, cement or varnish. The barium salt, though somewhat darker in color, possesses similar properties.

Precipitation of the calcium salt in the presence of water-soluble dyes leads to the formation of color lakes which are insoluble in water but soluble in other solvents, such as ethyl acetate or petroleum ether.<sup>87</sup> These lakes, and also those similarly prepared from the barium salt, may be employed in the manufacture of lithographic and printing inks, colored paints and varnishes.

Of the other metallic derivatives of these complex acids, the copper, chromium, and nickel salts which are green in color, and the cobalt salt, which is purple, may be employed in paints. The manganese salt is mahogany in color and hardens on exposure to air. Lead and zinc salts, though darker in color, possess properties somewhat similar to the corresponding barium and calcium compounds.

Naphthenic acids, obtained from the waste lyes in refining lubricating oils from Galician and Rumanian crudes, are described as brownish-black, resinous substances,<sup>88</sup> readily soluble in benzene. Samples of each exhibited acid numbers of 87 and 157, respectively. Metallic derivatives of some monocarboxylic naphthenic

<sup>85a</sup> G. Alleman, U. S. P. 1,931,855, Oct. 24, 1933, to Sun Oil Co.; *Brit. Chem. Abs.* B, 1934, 615.

<sup>86</sup> G. Alleman, U. S. P. 1,637,510, Aug. 2, 1927, to Sun Oil Co.; *Chem. Abs.*, 1927, 21, 3127.

<sup>87</sup> G. Alleman, U. S. P. 1,781,772, Nov. 18, 1930, to Sun Oil Co.; *Chem. Abs.*, 1931, 25, 420.

<sup>88</sup> F. Schwartz and J. Marcusson, *Chem. Rev. Fett-und Harzindustrie*, 1908, 15, 165; *Chem. Abs.*, 1908, 2, 2738. H. Burstin *Petroleum Z.*, 1921, 17, 1169; *Chem. Abs.*, 1922, 16, 1659, points out that dilute caustic alkali first extracts naphthenic acids from mineral oils, further extraction yielding resins. For the extraction of naphthenic acids from waste lyes obtained in refining Japanese petroleum, see Y. Tanaka and S. Nagai, *J. A. C. S.*, 1923, 45, 754. *J. Soc. Chem. Ind. Japan*, 1923, 26, 1115; 1926, 29, 115; *Chem. Abs.*, 1924, 18, 2332; 1926, 20, 2744. Y. Tanaka, K. Horiuchi and G. Oyama, *ibid.*, 1923, 26, 1190; *Chem. Abs.*, 1924, 18, 2638. Y. Tanaka, S. Nagai and S. Ishida, *ibid.*, 1924, 27, 810; *Chem. Abs.*, 1925, 19, 488. Y. Tanaka and T. Kuwata, *ibid.*, 1927, 30, 48; *Chem. Abs.*, 1927, 21, 1004.

acids, particularly the lead salts of trideca-, tetradeca-, and pentadeca-naphthenic acids from Japanese crudes, are resinous in appearance.<sup>39</sup>

In refining crude petroleum distillates, addition of sufficient alkali before distillation retains the natural emulsifying agents (naphthenic acids or acid resins) in the residues.<sup>40</sup> The latter may be dispersed directly in water, or acidified (to liberate the organic acids) and then emulsified in dilute caustic soda solution.

Materials resembling rubber or linnoxyn may be prepared in the following manner.<sup>41</sup> A slightly alkaline solution of an alkali naphthenate is treated with a solution of aluminum or chromium salts until a salt of hexanaphthenic acid (o-methylcyclopentanecarboxylic acid) begins to precipitate. In this way the unpleasant odor of the naphthenate is said to be removed. The naphthenates so obtained, when heated to 170°C., yield very viscous solutions resembling solutions of rubber. At higher temperatures (e.g., 300°C.) a horny mass is produced which gives mobile solutions in turpentine, pine oil and solvent naphtha.

Zernik<sup>42</sup> is of the opinion that the unpleasant odor associated with naphthenic acids is due possibly to low-boiling fractions and unsaponifiable constituents in the crude product. Such impurities can be eliminated by fractional distillation and treatment of the (naphthenic) soap solutions with inert solvents. Distillation involves cautious dehydration and fractionation in vacuo (without superheated steam) from vessels containing aluminum cooling coils. Salts of the purified acids may be employed in making resins and lacquers.

A number of metallic salts of naphthenic acids have been proposed for various purposes. For example, lead salts are suggested as driers for varnishes,<sup>43</sup> those of aluminum and chromium as siccatives,<sup>44</sup> and others such as iron, zinc or calcium for improving the properties of electrical insulating materials,<sup>45</sup> or when mixed with fillers (e.g., lithopone, cork meal, sawdust or powdered metals) for the manufacture of artificial leather, sealing wax or adhesives.<sup>46</sup> Other uses for metallic naphthenates include incorporation with ceresin or paraffin or carnauba wax to yield synthetic resins and waxes,<sup>47</sup> addition to lubricating or other oils to increase their viscosity<sup>48</sup> and act as antioxidants,<sup>49</sup> as emulsifying agents for petroleum distillates<sup>50</sup> and residues,<sup>51</sup> and catalysts for the polymerization of drying or semi-drying oils.<sup>52</sup> Calcium naphthenate is said to be a stabilizing agent for coating compositions containing a polysaccharide ester and an alkyl naphthenate.<sup>53</sup> Condensation products of naphthenic acids and amino-alcohols (for example, mono-, di- or tri-ethanolamine) may be employed as dispersing agents in the dyeing of

<sup>39</sup> Y. Tanaka, K. Horiuchi and G. Oyama, *J. Chem. Ind. (Japan)*, 1923, 26, 1190, *Chem. Abs.*, 1924, 18, 2688.

<sup>40</sup> British P. 302,346, 1928, to Bataafsche Petroleum Maatschappij, *Brit. Chem. Abs. B*, 1930, 312.

<sup>41</sup> G. Ruth and E. Asser, German P. 327,913, 1919; *J. S. C. I.*, 1921, 40, 188A.

<sup>42</sup> F. Zernik, *Erdöl u. Teer*, 1925, 1; *Chem. Abs.*, 1926, 20, 2743. Also, U. S. P. 1,537,572, May 12, 1925, *Chem. Abs.*, 1926, 20, 513.

<sup>43</sup> Geiman P. 510,937, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1108.

<sup>44</sup> G. Ruth and E. Asser, German P. 327,374 and 327,375, 1919; *J. S. C. I.*, 1921, 40, 187A.

<sup>45</sup> British P. 318,412, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 901. German P. 482,366, 1928; *Chem. Abs.*, 1930, 24, 447.

<sup>46</sup> F. Pohl, German P. 383,815, 1921, to C. Jäger G. m. b. H.; *J. S. C. I.*, 1924, 43, 303B.

<sup>47</sup> F. Zernik, German P. 388,289, 1921, to Erdöl- & Kohle-Verwertung A.-G.; *J. S. C. I.*, 1924, 43, 392B.

<sup>48</sup> E. A. Rudiger, Canadian P. 265,727, 1928; *Chem. Abs.*, 1927, 21, 1007. L. L. Rehber, U. S. P. 1,582,227, April 27, 1926, to Union Oil Co. of Calif.; *Chem. Abs.*, 1926, 20, 2067. DeR. Frizell, U. S. P. 1,582,258, April 27, 1926, to Union Oil Co. of Calif.; *Chem. Abs.*, 1926, 20, 2067.

<sup>49</sup> T. Yamada, *J. Soc. Chem. Ind. Japan*, 1930, 33, 318, 319; *Chem. Abs.*, 1930, 24, 5996, 5997.

<sup>50</sup> DeR. Frizell and B. A. Stagner, U. S. P. 1,582,237, Mar. 27, 1926, to Union Oil Co. of Calif.; *Brit. Chem. Abs. B*, 1926, 573.

<sup>51</sup> R. Lichtenstern, British P. 263,975, Nov. 3, 1925, to "Allchemin" allgem. chem. Ind. A.-G.; *Brit. Chem. Abs. B*, 1927, 190.

<sup>52</sup> G. Petrov, British P. 214,679, 1922; *Chem. Abs.*, 1924, 18, 2520.

<sup>53</sup> S. Hori, U. S. P. 1,829,750, Nov. 3, 1931; *Chem. Abs.*, 1932, 26, 816. Calcium naphthenate has been employed also to stabilize cellulose esters and ethers. British P. 423,044, 1934, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B*, 1935, 320.

cellulose acetate fabrics.<sup>54</sup> Arylamino derivatives have been prepared by the reaction of aromatic amines on naphthenic acids.<sup>55</sup> The latter acids, in chloroform solution, react also with hydrazoic acid to yield amines.<sup>56</sup>

Naphthenic acid anhydrides, made by heating the acids with acetic anhydride, are soluble in ether and benzene but very much less so in cold 95 per cent alcohol than naphthenic acids.<sup>57</sup> The anhydrides react with cellulose, in the presence of pyridine, to give the corresponding esters.

#### RESINS BY OXIDATION OF PETROLEUM

Oxidation of petroleum and petroleum distillates gives rise to a wide variety of products including resins and asphaltic materials, depending upon the conditions of oxidation. Thus far, however, no high-grade resin appears to have been made by such methods. Brooks<sup>58</sup> considers that in view of the nature of copal acids and those of other natural resins, there is a distinct promise that polycyclic hydrocarbons of lubricating oil distillates and the heavier fractions of gas oil can be oxidized to resins. No such procedure has been developed yet which does not give black asphaltic products.

From the viewpoint of synthetic resins, the most interesting reactions are those yielding asphaltenes and asphalt-like bodies and carboxylic acids. Vapor-phase oxidation of heavy petroleum distillates gives acids of the aldehyde or hydroxy-aldehyde type mixed with aldehydes of various molecular weights. On saponification with alkalis, brown or yellow resins are formed by condensation.<sup>59</sup> If the soaps are separated and treated with an excess of dilute hydrochloric acid, resinification of the liberated acids takes place.<sup>60</sup> These latter resins are suggested as bases for paint and varnish mixtures.

Resinifiable acids are obtained by catalytic oxidation of hydrocarbon oils in the liquid-phase. For example, by air-blowing petroleum in the presence of alkalis Schaal<sup>61</sup> obtained liquid acids which, on vacuum distillation, furnished a residue of a resinous nature. Solid acids from this same procedure formed asphalt-like masses with calcium or magnesium oxides. Esters of the latter acids were somewhat resinous in character and could be used in making varnishes or as substitutes for waxes, pitch or asphalt. Charitschoff<sup>62</sup> points out that Schaal's method yields not only naphthenic acids but also viscous polynaphthenes which are probably bicyclic condensation products. These polynaphthenes seem to be pseudo-acids, apparently tribasic although they contain only four atoms of oxygen. As they are easily decomposed to resinous substances by heat or the action of concentrated alkaline solutions they have been called asphaltogenic acids.

High-boiling petroleum fractions (lubricating distillates, turbine or transformer oils) give resins and asphaltic substances, which are either neutral or acid in character, on exposure to air. Three classes are recognized in the case of lubricating oils;<sup>63</sup>

<sup>54</sup> H. Dreyfus, British P. 394,657, 1933; *Chem. Abs.*, 1934, 28, 272

<sup>55</sup> French P. 711,952, 1930, to Soc. prod. chim. et matieres colorantes de Mulhouse; *Chem. Abs.*, 1932, 26, 1943.

<sup>56</sup> K. F. Schmidt and S. Strzygowski, German P. 500,435, 1928, to Knoll A.-G. chem. Fabrik; *Chem. Abs.*, 1932, 26, 2198. K. F. Schmidt, German P. 544,890, 1930, to Knoll A.-G. chem. Fabrik; *Chem. Abs.*, 1932, 26, 3315.

<sup>57</sup> G. Kita, T. Mazume, J. Sakurada and T. Nakashima, *Kunststoffe*, 1926, 16, 167; *Chem. Abs.*, 1927, 21, 320.

<sup>58</sup> B. T. Brooks, *Ind. Eng. Chem.*, 1924, 16, 189.

<sup>59</sup> J. H. James, U. S. P. 1,681,237 and 1,681,238, Aug. 21, 1928, to C. P. Byrnes; *Brit. Chem. Abs.*, B, 1928, 865.

<sup>60</sup> J. H. James, U. S. P. 1,894,352, July 17, 1933, to C. P. Byrnes; *Brit. Chem. Abs.* B, 1933, 904.

<sup>61</sup> E. Schaal, German P. 22,705, 1884. British P. 12,806, 1884; *J.S.C.I.*, 1885, 4, 679.

<sup>62</sup> K. W. Charitschoff, *Chem.-Ztg.*, 1909, 33, 1165. *J. Russ. Phys.-Chem. Soc.*, 1908, 40, 1413, 1757; *J.C.S.*, 1909, 96 (1), 184. *J. Russ. Phys.-Chem. Soc.*, 1909, 41, 345; *J.C.S.*, 1909, 96 (1), 471.

<sup>63</sup> J. C. Jennings, *J.C.S.I.*, 1923, 48, 1180. See also T. S. Eligh, Jr., *Proc. A.S.T.M.*, 1924, 24 (2), 964; *Chem. Abs.*, 1923, 19, 1491.



(1) Asphaltic resins, soluble in oil and petroleum ether and absorbed by charcoal and fuller's earth, which are responsible for the discoloration and increase in viscosity of the oil.

(2) Asphaltenes, which are insoluble in petroleum ether and are formed by oxidation of the resins.

(3) "Varnish," which is the final oxidation product and is insoluble in all the usual solvents.

It is doubtful, however, whether the above classification is complete since acidic resins are often produced. In the sludging of turbine oils, for example, complex naphthenic acids probably containing hydroxy, keto, or aldehydic groups are formed. A turbine oil sludge investigated by Salathe<sup>94</sup> contained 13.6 per cent of complex naphthenic acids having 50 or more carbon atoms per molecule. In the dry state these acids were brown, hard, brittle resins and were soluble in the lower aliphatic alcohols, chloroform, pyridine, aniline, benzene and slightly soluble in ether. The calcium salt was obtained as a brown gelatinous precipitate.

Oxidation of tar oil, paraffin, or montan wax also furnishes acids of high molecular weights. By treating tar oil (free of phenol) at 200°C. with air under 30 atmospheres pressure, in the presence of sodium carbonate, Schneider<sup>95</sup> secured a 55 per cent yield of liquid syrupy acids whose properties were similar to those of Charitschoff's polynaphthenic acids. In the absence of alkali about one-half of the tar oil was precipitated as a solid asphalt. Lignite tar gave mainly monobasic fatty acids. Using 200 g. of paraffin, 800 cc. of 2.5*N* sodium carbonate solution, 30 atmospheres pressure, a temperature of 170°C. and 200 l. of air per hour, 141 g. of paraffin were oxidized giving 46 per cent of water-insoluble acids. These were brown in color and had an average molecular weight of 271. From American paraffin, acids of the formula  $C_nH_mO_2$  ( $n = 13, 15, 17$  or  $19$ ) were obtained. In the latter instance, reaction was accelerated by salts of iron, copper and manganese, but not by alkalis. Montan wax was difficult to oxidize and yields were low. Schmidt<sup>96</sup> exposed paraffin wax to a blast of air for a considerable period of time at 100-120°C., producing resin acids and fatty acids. Rapidity of reaction is increased by addition of mercuric oxide or previously oxidized wax.

Chernozhukov<sup>97</sup> states that the oxidation products (of petroleum) having acid values between 60 and 110 form resinous bodies by loss of carbon dioxide and subsequent condensation of the resulting unsaturated hydrocarbons. Also condensation of aldehydes and other intermediate oxidation compounds may take place. Reaction of acids with aldehydes in the presence of amines is a method suggested by Petrov.<sup>98</sup>

The dark-colored liquids obtained by pressing crude acids (from oxidation of paraffin wax) are acidic in character and insoluble in petroleum ether. These may be combined with glycerol, or other polyhydric alcohols, to give materials resembling linnoxyn or artificial rubber.<sup>99</sup> Catalysts, e.g., lead oxide or sulphur, may be used also. To illustrate, 150 parts of the liquid acids are mixed with 19.3 parts of glycerol and heated for 30 minutes at 170-210°C. A dark, tenacious, non-greasy elastic mass is formed which is soluble in alcohol, petroleum ether and acetone. Addition of 15 parts of sulphur to the above mixture before heating results in a deep-black, crumbly mass. The liquid acids may be substituted by unsaturated aliphatic acids made by dehydration of the oxidation products of paraf-

<sup>94</sup> A. Salathe, *Ind. Eng. Chem.*, 1925, 17, 414.

<sup>95</sup> W. Schneider, *Brennstoff-Chem.*, 1920, 1, 70, 80; *Chem. Abs.*, 1921, 15, 743.

<sup>96</sup> A. Schmidt, *British P.* 142,507, 1920; *J.S.C.I.*, 1921, 40, 74A.

<sup>97</sup> N. I. Chernozhukov, *Izvestia Thermo-Chem. Inst., Moscow*, 1928, 6, 7; *Brit. Chem. Abs. B.*, 1929, 955.

<sup>98</sup> G. S. Petrov, *Russian P.* 24,585, 1931; *Chem. Abs.*, 1932, 26, 2334. *Russian P.* 27,468, 1931; *Chem. Abs.*, 1933, 27, 2321.

<sup>99</sup> M. Luther and R. Held, *U. S. P.* 1,884,023 and 1,884,024, Oct. 25, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1222.

fin hydrocarbons or waxes.<sup>70</sup> Reaction then takes place best in the presence of a solvent, such as a petroleum distillate. Air or oxygen may be passed into the mixture during heating.

Artificial shellac is prepared by Burwell<sup>71</sup> in the following manner:

A fuel oil distillate, of 33-18° Bé, is oxidized at 130-160°C. and 150-350 atmospheres pressure with air or oxygen-enriched air. About 0.1 per cent of iron, copper, or manganese oleate is used as catalyst. The initial products of the reaction consist of petroleum-soluble acids and petroleum-insoluble hydroxy acids.<sup>72</sup> Reaction is continued until the concentration of the latter reaches 20-40 per cent. Three layers are formed, the top consisting of unchanged hydrocarbons and petroleum-soluble oxidation products and the bottom of an aqueous solution of acids. The middle layer containing hydroxy acids is separated and distilled at a pressure of 10-20 mm. and temperature of 140-275°C to remove the more volatile constituents. Employment of the higher distillation temperatures furnishes harder and more brittle resins, but the less brittle, even tacky, resins have significant dielectric properties.

Air-blowing of alberta bitumen results in the formation of rubber-like products.<sup>73</sup> During blowing there is a decrease in the proportions of asphaltous acids and anhydrides, oily constituents and resins, and an increase in the melting point of the material. At the same time the molecular weight of the resins increases from 733 to 1012 and that of the asphaltenes from 2219 to 4690. Reactions appear to be essentially dehydrogenation, i.e., removal of hydrogen as water, followed by polymerization. The latter is accelerated by the sulphur content of the bitumen.

The possibility of preparing resins from high-boiling petroleum distillates by treatment with ozone is indicated by the work of Koetschau.<sup>74</sup> By subjecting a transformer oil (sp.gr. 0.915 and molecular weight, in benzene, 293) to the action of ozone at 12°C. a 25 per cent yield of ozonides was obtained. These were solid or semi-solid substances, insoluble in petroleum ether and having a mean molecular weight of 663. The latter figure corresponds closely with the calculated value of the dimeric ozonide,  $(C_{10}H_{20}O_6)_2$ . Unless kept at low temperatures, the ozonides decompose and redden. Ozonization of spindle oils, from Texas and Pennsylvania crude oils, yielded a flocculent, white precipitate which, at temperatures of 21°C. or higher, gradually changed to a red-colored resin. Stable products were obtained from oils previously refined with aluminum chloride, the latter procedure removing a large proportion of the sulphur compounds.

Mention has been made of the important role played by sulphur compounds in the formation of asphaltenes from heavy oils.<sup>75</sup> Sludge formation in transformer oils by oxidation apparently is markedly accelerated by salts of sulphonic acids.<sup>76</sup> Certain metals, for example, copper and lead, increase the rate of development of both resins and sludge in the same types of oil.<sup>77</sup> The changes taking place in petroleum residues and tars on blowing with air were investigated by Marcusson and Picard.<sup>78</sup> Oxidation and polymerization were not influenced by catalysts such as manganese dioxide or fuller's earth possibly because the latter were poisoned by sulphur compounds.

<sup>70</sup> British P. 327,094, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5172.

<sup>71</sup> A. W. Burwell, U. S. P. 1,770,875 and 1,770,876, July 15, 1930, to Alox Chem. Corp.; *Chem. Abs.*, 1930, 24, 4647. British P. 309,383 and 307,384, 1917; *Chem. Abs.*, 1930, 24, 717. German P. 568,267, 1928; *Chem. Abs.*, 1933, 27, 2052.

<sup>72</sup> Similar acids are found as lacquer deposits within Diesel engines. The formation of the lacquer is attributed to incomplete combustion: C. A. Bouman, *Proc. World Pet. Congr.*, 1933, 2, 248; *Brit. Chem. Abs. B*, 1934, 1046.

<sup>73</sup> M. Katz, *Can. J. Res.*, 1934, 10, 435; *Brit. Chem. Abs. B*, 1934, 562.

<sup>74</sup> R. Koetschau, *Chem.-Ztg.*, 1921, 45, 466; *Chem. Abs.*, 1921, 15, 2717.

<sup>75</sup> A. I. Chernozhukov, *loc. cit.* See also C. E. Waters, *Ind. Eng. Chem.*, 1922, 14, 725.

<sup>76</sup> G. L. Stadinikov and Z. I. Vozninskais, *Trans. Karpov Chem.*, 1926, 5, 109; *Chem. Abs.*, 1928, 22, 2049. *Neft. Khoz.*, 1927, 12, 694; *Chem. Abs.*, 1928, 22, 4240. *Petroleum Z.*, 1929, 25, 651; *Chem. Abs.*, 1929, 23, 4336.

<sup>77</sup> H. Stager, *Schweiz Elektrotech. Ber. Bull.*, 1924, 15, 93; *Chem. Abs.*, 1925, 19, 724. H. von der Heyden and K. Typke, *Petroleum*, 1924, 20, 320, 337, 953.

<sup>78</sup> J. Marcusson and M. Picard, *Chem.-Ztg.*, 1924, 48, 335.

Resinous substances are produced by oxidation of petroleum hydrocarbons with certain chemical reagents. When liquid paraffin of the German Pharmacopoeia is oxidized in sulphuric acid with potassium permanganate a soft resin is obtained. If first oxidized in alkaline solution with permanganate and then further in acid solution a brittle resin softening at 75°C. is formed. This resin is partly soluble in hot caustic potash solution, is easily soluble in benzene, chloroform, turpentine, ether, alcohol and acetone, and is difficultly soluble in carbon tetrachloride, methyl alcohol and heavy benzene.<sup>79</sup> Chlorine resinifies paraffin oil, addition of potassium bichromate favoring the production of solid material. If bichromate and hydrochloric acid are used, the reaction is likely to become violent and requires careful attention. By heating 2 parts of liquid paraffin oil with 2.5 parts of nitric acid (sp.gr. 1.486) for 10 hours at 90-100°C., then adding 0.5 part of nitric acid and heating for 2 hours longer, solids were obtained. These, when dissolved in 15 per cent caustic potash solution and acidified with hydrochloric acid, gave a 75 per cent yield of resinous brown fatty acids. By employing this same procedure, paraffin wax yielded a mass of ointment-like consistency. Yellow vaseline furnished both a solid and an ointment-like resin, the latter containing no acid constituents.

After partial neutralization and esterification of the acids in montan wax, resulting from bleaching with chromic acid, the mass can be incorporated with iron powder to give products applicable to the manufacture of magnetic cores.<sup>80</sup> A varnish, which however is not very fast to moisture, is made by dissolving the calcium salt of oxidized vaseline in turpentine.<sup>81</sup>

The work of Bestuzhev<sup>82</sup> indicated that mild oxidation of lubricating oils with nitric acid converted the naphthenic constituents mainly to acids. When concentrated nitric acid and elevated temperatures were employed oxidation was more energetic and yielded polymerization products, resins and asphaltic compounds.

According to Kleiber and Gilardi<sup>83</sup> a type of synthetic rubber is made in the following manner:

Five l. of American petroleum are agitated for 4 hours with 1.25 l. of nitric acid (sp.gr. 1.4). The reaction mixture is washed with water and alkali, and repeatedly distilled from rosin. The residue may be used as a substitute for copal. The distillate is heated with alkali (125 g. of sodium hydroxide in 1.25 l. of water) at 156°C. and a pressure of 5-6 atmospheres for 1 hour. Three layers are formed. To 5 l. of a mixture of the two upper layers, at 40°C., are added 2 kg. of acetic acid and 1.25 l. of formaldehyde, in small portions, followed by 350 g. of crude rubber. Heating is continued for 8 hours at 60°C. Treatment of the resulting syrupy liquid with 4 volumes of acetone or alcohol precipitates a vulcanizable, elastic mass.

Rubber-like bodies may be obtained by oxidation of hot oil or pitch with air in the presence of an oxygen-transmitter such as the oxides of nitrogen.<sup>84</sup> A catalyst, e.g., nitric acid and a little manganese dioxide may be employed also.

#### RESINS BY CONDENSATION WITH VARIOUS REAGENTS

**Reaction with Formaldehyde.** Reaction of certain cyclic and unsaturated hydrocarbons with formaldehyde, in the presence of sulphuric acid, gives the so-

<sup>79</sup> A. Langer, *Chem.-Ztg.*, 1921, 45, 466; *Chem. Abs.*, 1921, 15, 2717.

<sup>80</sup> K. Eisenmann and F. Bergmann, U. S. P. 1,783,560, Dec. 2, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 389. British P. 320,016, 1928; *Chem. Abs.*, 1930, 24, 2847.

<sup>81</sup> S. Vedenkin, *Malyarnoe Delo*, 1931, (3), 26; *Chem. Abs.*, 1932, 26, 5219.

<sup>82</sup> M. Bestuzhev, *Erdöl u. Teer*, 1931, 7, 205; *Chem. Abs.*, 1931, 25, 3816.

<sup>83</sup> E. Kleiber and P. Gilardi, British P. 312,741, 1928; *Brit. Chem. Abs. B*, 1929, 652. French P. 36,588, 1929, addn. to 651,824, 1928; *Chem. Abs.*, 1929, 23, 3600; 1930, 24, 6065.

<sup>84</sup> K. W. Nielsen, Danish P. 33,940, 1924; *Chem. Abs.*, 1925, 19, 1508. British P. 229,690, 1925; *J S C I.*, 1925, 44, 873B.

called "formolites" which are solids, often of a resinous nature.<sup>85</sup> This reaction was discovered by Nastuykov,<sup>86</sup> who proposed it as a quantitative method for the determination of aromatics. The test as originally advocated by Nastuykov involved mixing the petroleum distillate with an equal volume of concentrated sulphuric acid, the latter being added in small portions, and then adding slowly with good agitation one and a half volumes of aqueous formaldehyde. A precipitate was formed which after washing with petroleum ether and ammonia water was a brown powder. These proportions were satisfactory when the formolite was less than 50 per cent of the weight of the oil; if greater, then the proportions of reactants suggested were 1:1:2.<sup>87</sup> If less sulphuric acid was employed the product varied in character from the usual amorphous insoluble powder through soluble solid to soluble liquid materials. Highest yields were obtained by carrying out the reaction at about 0°C.<sup>88</sup>

The above procedure was modified later,<sup>89</sup> and proportions of oil, acid and formalin were changed to 1:4:2. After condensation, the mixture was refluxed on a water bath for 1 hour, and then diluted with 5 volumes of water. Any clear supernatant oil was withdrawn. After heating again for 1 hour, in a current of steam, the precipitate was filtered, washed and neutralized as before, dried and weighed. To the weight in grams add 5.25 per cent (to account for persistence of moisture and change in weight due to reaction with formalin) to obtain formolite numbers. Such alterations in method are said to yield a powder-like mass which is never sticky. The solubility of formolites in benzene and their insolubility in other solvents (alcohol, chloroform, carbon tetrachloride, acetone and ether) appear to increase with the boiling point of the oil.<sup>90</sup>

Severin<sup>91</sup> investigated the effects of the sulphuric acid-formaldehyde mixture on different types of hydrocarbons. Paraffins (normal hexane or octane) and saturated naphthenes (methyl or dimethylcyclohexane) did not react with this reagent. Olefins (amylene or octylene) yielded a reddish-brown syrupy liquid and unsaturated naphthenes (cyclohexane or dimethylcyclohexane) gave reddish-brown precipitates soluble in water. Aromatics formed water-insoluble precipitates which were red in color except those from naphthalene and anthracene, which were deep green and yellowish green, respectively. It was suggested that olefins be removed from petroleum fractions (boiling below 200°C.) with 3 per cent of sulphuric acid before formolite numbers are determined. Also distillates with a high content of aromatics should be diluted with paraffinic benzine.<sup>92</sup>

Tauss<sup>93</sup> reports that conjugated diolefins, e.g., methylbutadiene, respond to the formolite reaction. Completely substituted aromatics, such as hexamethyl- or hexaethylbenzene, do not yield formolites, thus apparently indicating that only hydrogen atoms attached to the benzene nucleus combine with formaldehyde. He also proposed the use of trioxymethylene instead of aqueous formaldehyde as the latter so dilutes the sulphuric acid as to impair its value as a condensing agent.<sup>94</sup>

<sup>85</sup> Some German chemists comprehend under the term formolite all resins yielded by the action of formaldehyde on any substance capable of reacting with this aldehyde to form resinous bodies. The resinifying reactions of formaldehyde are so varied and the products so diverse, physically and chemically, that such a classification is considered by the author to lead to much confusion.

<sup>86</sup> A. M. Nastuykov, *J. Russ. Phys.-Chem. Soc.*, 1904, 36, 881; *J.C.S.*, 1904, 86 (1), 801. *Trud. bakur. tech. Ges.*, 1908, 5. A. M. Nastuykov and N. V. Gurin, *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 46; *Chem. Abs.*, 1915, 9, 1471.

<sup>87</sup> A. M. Nastuykov, *Petroleum*, 1909, 4, 1336; *Chem. Abs.*, 1910, 4, 247.

<sup>88</sup> A. M. Nastuykov, *Petroleum*, 1911, 7, 239.

<sup>89</sup> A. M. Nastuykov, *J. Ind. Chem. (Russia)*, 1925, 1, 23; *Chem. Abs.*, 1926, 20, 498.

<sup>90</sup> K. Kostin, *Neft. Khoz.*, 1925, 8, 579; *Chem. Abs.*, 1927, 21, 1703.

<sup>91</sup> E. Severin, *Mon. du petrole Roum.*, 1911, 21, 22; *Chem. Abs.*, 1911, 5, 3904.

<sup>92</sup> Dilution with aliphatic benzine to minimize over-heating is recommended by J. Marcusson (*Chem.-Ztg.*, 1911, 35, 729) and B. Tarasov and V. Rudenko (*Neft. Khoz.*, 1926, 10, 245); *Chem. Abs.*, 1927, 21, 2554.

<sup>93</sup> J. Tauss, *J. prakt. Chem.*, 1919, 99, 276; *Chem. Abs.*, 1920, 14, 934.

<sup>94</sup> A critical analysis of the formolite reaction is given by J. Hosek, *Chem. Obzor.*, 1929, 4, 67; *Chem. Abs.*, 1929, 23, 2813.

It is interesting to note that the procedure of Richardson,<sup>96</sup> in which trioxymethylene is employed, gives rise to a gummy material insoluble in concentrated ammonium sulphate solution but soluble in water.<sup>96</sup>

A further modification of the formolite reaction is proposed by which various properties of the oil can be determined.<sup>97</sup> The first formolite number,  $F_1$ , is obtained as previously described. The second number,  $F_2$ , is obtained by treating the first formolite with petroleum ether in the cold, filtering, drying at 100-105°C. and weighing.  $F_1 - F_2$ , or  $a$  is the true potential content of lubricating oil. The second formolite is treated in the same way with chloroform to give  $F_3$ , or the real formolite number.  $F_2 - F_3$ , or  $b$ , represents the resin content of the oil. Formolite values up to  $F_7$  are calculated. Differences between these indicate the proportions of total unsaturated cyclic hydrocarbons, light lubricating fractions, asphaltic unsaturated hydrocarbons and saturated hydrocarbons. The Engler viscosity,  $E$ , may be calculated according to the formula

$$\frac{(E + b)}{(F_2 + 2b - 3.5)} = C$$

in which the values of  $C$  (a constant), at 100°C. for cylinder oils and "viscosines" and at 50°C. for machine oils, are 0.20, 0.22 and 0.29, respectively.

Formolites are obtained by treating (unsaturated) fractions from the distillation of *Ostaschkov sapropel*<sup>98</sup> with an equal volume of concentrated sulphuric acid and 0.5 volume of 40 per cent formalin.<sup>99</sup> These are brown, amorphous products, insoluble in organic solvents and have no definite melting points. Such resins from sapropels are suggested as electrical insulating materials, as they are reported to possess the property of adhering to metals without cracking when the latter are bent.<sup>100</sup>

Application of the formolite reaction in the refining of lubricating or burning oils is described by Nastyukov.<sup>101</sup> The crude distillate is treated with a mixture of 4 volumes of sulphuric acid and 2 volumes of 40 per cent formaldehyde. The reaction mass is diluted with water, steam distilled to remove volatile products, and filtered. The precipitate is washed, neutralized and dried and the resulting brown powder freed of adsorbed oil by extraction with benzene. This formolite, alone or mixed with synthetic resins or other plastics, may be employed in the manufacture of molded articles.<sup>102</sup>

Ormandy and Craven<sup>103</sup> found when cracked gasolines are refluxed with formalin, in the presence of an electrolyte, brown resins are formed. These varied in consistency from a sticky oil to a hard gum. A typical reaction mixture consisted of 5 g. of gasoline, 5 cc. of formalin and 5 cc. of hydrochloric acid (sp.gr. 1.16). Heating for about 2 hours was necessary. The reaction product was isolated by evaporation of the gasoline and drying the residue in a steam-oven. Yields were roughly proportional to the bromine number of the hydrocarbon liquid, though small amounts of resins were obtained from benzene and its immediate homologues. Condensa-

<sup>96</sup> C. Richardson, *Ind. Eng. Chem.*, 1916, 8, 319.

<sup>97</sup> A. Holmes, *Ind. Eng. Chem.*, 1924, 16, 258.

<sup>98</sup> A. M. Nastyukov, *Petroleum Z.*, 1926, 22, 1349; *Chem. Abs.*, 1927, 21, 1538. *Petroleum Z.*, 1927, 23, 1451; *Brit. Chem. Abs. B*, 1928, 148.

<sup>99</sup> *Sapropel* is a naturally occurring oily or wax-like decomposition product of marine plants and animals: L. Litinsky, *Petroleum-Z.*, 1921, 17, 437; *Chem. Abs.*, 1921, 15, 3739. Kukuk, *Brennstoff-Chem.*, 1921, 2, 305; *Chem. Abs.*, 1922, 16, 543. H. Potonie, *Ber. deut. pharm. Ges.*, 1907, 17, 180; *Chem. Zentr.*, 1907, 2, 555.

<sup>100</sup> W. Walgis, *Neft. Khoz.*, 1925, 9, 290; *J.S.C.I.*, 1925, 44, 836B.

<sup>101</sup> N. Zelinski and B. Maxarov, *Neft. i. slanc. Khozajstvo*, 1925, 8, 945; *Brit. Chem. Abs. B*, 1926, 121.

<sup>102</sup> A. M. Nastyukov, *British P.* 289,920, 1927; *Chem. Abs.*, 1929, 23, 968.

<sup>103</sup> A. M. Nastyukov, German P. 500,305, 1927; *Chem. Abs.*, 1931, 25, 784. Cf. O. Katstov, *Plasticheskie Massy*, 1934 (1), 28; *Chem. Abs.*, 1934, 28, 6000.

<sup>104</sup> W. R. Ormandy and E. C. Craven, *J. Inst. Pet. Tech.*, 1924, 10, 99.

tion with formaldehyde converted only a part of the unsaturated hydrocarbons to resins in one treatment. An increase in the proportion of formalin, or substitution of formalin by paraformaldehyde, resulted in a smaller yield of products. Some of the results obtained by these investigators are given in Table 24.

TABLE 24.—Resins from Cracked Gasoline and Formaldehyde.

	Bromine No.	Yield of Resin, %
Cracked Gasoline No. 1 .	76 2	35 8
Cracked Gasoline No. 2 .	21 6	6 9
Cracked Gasoline No. 3 .	70 6	37 2
Cracked Gasoline No. 4 .	64 5	27 5
Cracked Gasoline No. 5 .	20 0	4 2
Cracked Gasoline No. 6 .	83 2	54 0
Cracked Gasoline No. 7 .	59 3	26 2
Benzene . . . . .	0 2	0 5
Toluene . . . . .	Nil	1 5
m-Xylene . . . . .	Nil	6 8

**Reaction With Methylal.** According to Herr,<sup>104</sup> methylal yields condensation products of the formolite type with the aromatic constituents of petroleum or its distillates. Methylal is said to be superior to formaldehyde because it acts as a solvent as well as a condensing agent and is more sensitive, being capable of detecting 0.05 per cent of benzene.

One part by weight of the oil dissolved in 2 parts of methylal and 4 parts of sulphuric acid introduced as a fine stream gives a product which is separated by pouring the liquid mixture into water, neutralizing with ammonia and filtering. If the liquid is kept cool during reaction, the product is soluble in chlorobenzene. On the other hand if the liquid is allowed to become hot and finally is heated on a water bath for half an hour, a large yield of an insoluble material is obtained. A rough rapid comparative determination of the unsaturated constituents of an oil can be made by taking a 2 cc. sample in a graduated stoppered bottle, adding 4 cc. of methylal dissolved in 10 cc. of light petroleum, then 2 cc. of sulphuric acid and shaking for one minute. After standing for half an hour, the volume of the precipitate is read directly.

An investigation of the formolite reaction was made by Dobryanski,<sup>106</sup> using a solution of 1 g. of benzene in 9 cc. of benzene, and methylal instead of formaldehyde. The optimal proportion of reactants was 5 cc. of methylal, 7.5 cc. of 93.6 per cent sulphuric acid and 10 cc. of the benzene solution. The highest formolite number was obtained in 10 minutes, and an excess of the acid should be avoided. Formolites differed qualitatively according to the conditions and proportions of reactants. The condensation product obtained when the quantity of mixture employed was considerably less than that mentioned above was designated  $\alpha$ -formolite. The dark-colored condensate obtained by treatment with an excess of sulphuric acid was called  $\gamma$ -formolite. This became a horn-like mass when dried.  $\beta$ -Formolite was secured under optimal conditions. The high sensibility of the formolite number against the quantity and concentration of aromatic hydrocarbons renders the determination of the latter in unknown mixtures problematical. At best the number can be used for comparative purposes only.

**Reaction With Metallic Halides.** Anhydrous stannic chloride<sup>106</sup> polymerizes oxygenated bituminous constituents of petroleum. Only a small amount of the reagent is required to produce a bulky precipitate from a heavy crude distillate. This chloride converts tars into solid asphaltum or pitch-like substances. For ex-

<sup>104</sup> V. F. Herr, *Chem.-Ztg.*, 1910, 34, 893; *J.S.C.I.*, 1910, 29, 1094. See also M. Borodulin, *Neft Khoz.*, 1923, 14, 393; *Chem. Abs.*, 1923, 22, 2262.

<sup>105</sup> A. Dobryanski, *Neft Khoz.*, 1927, 12, 57; *Chem. Abs.*, 1928, 22, 4239. Cf. A. Dobryanski and M. Olevskii, *Neft Khoz.*, 1927, 12, 227; *Chem. Abs.*, 1928, 22, 4240.

<sup>106</sup> G. Torossian, *Ind. Eng. Chem.*, 1921, 13, 904.

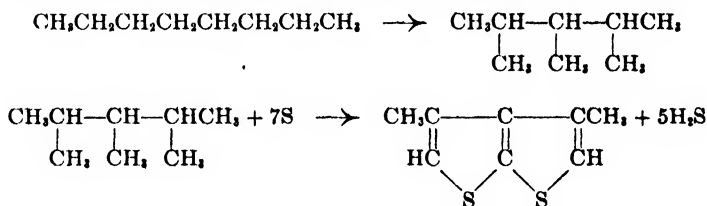
ample, pine tar is changed into a solid, lustrous, pitch-like body on treatment with 10-15 per cent of stannic chloride. Reaction is very vigorous and highly exothermic.

As previously mentioned, leNobel<sup>107</sup> employed ferric chloride, anhydrous aluminum chloride or boron fluoride to eliminate asphaltenes, as amorphous insoluble materials, from asphalt. Other halides suggested as precipitants for asphaltic or gummy compounds from lubricating oils include titanium chloride, zinc chloride and stannic bromide dissolved in liquid sulphur dioxide.<sup>108</sup>

Stable resins are prepared in the following manner from petroleum tar.<sup>109</sup> The tar is distilled at low pressures (1 mm.) to remove oily material and the residue is treated for 2 hours at 100-180°C. with 1-10 per cent of aluminum chloride. Reactive constituents are condensed or polymerized. The resin is purified either by extraction with a selective solvent or by treating its solution in a hydrocarbon solvent with sulphuric acid and evaporating the solvent after neutralizing.

Zelinskii and Smirnov<sup>110</sup> heated the heptanaphthene fraction (b.p. 101-102°C. at 740 mm.) from Baku petroleum with aluminum chloride in sealed tubes to temperatures of 100-140°. The reaction products consisted of a gas (mainly isobutane), high-boiling liquid unsaturated hydrocarbons and a yellow non-distillable resin.

**Reaction With Sulphur and Sulphur Chloride.**<sup>111</sup> When saturated hydrocarbons are heated with sulphur to temperatures above 200°C. reaction occurs yielding hydrogen sulphide and resinous and asphaltic substances of unknown constitution. Though some cyclic hydrocarbons, such as cyclohexane, are stable to sulphur at temperatures up to 200°C. many high-molecular-weight hydrocarbons and heavy petroleum distillates are vigorously attacked under these conditions.<sup>112</sup> Indications are that both condensation and dehydrogenation reactions take place.<sup>113</sup> For example, cyclic sulphur-containing compounds are obtained by heating sulphur and octane in sealed tubes to 270-280°C. Their formation may be represented by:



Under similar conditions hexylene and sulphur gave the following compounds:  $\text{C}_6\text{H}_{12}\text{S}$ , boiling point 40-41°C. at 10 mm.;  $\text{C}_8\text{H}_{16}\text{S}$ , boiling point 112-113°C. at 10 mm.;  $\text{C}_{10}\text{H}_{20}\text{S}$ , boiling point 128°C. at 10 mm.; and an asphaltic residue whose composition corresponded to the formula,  $\text{C}_{24}\text{H}_{32}\text{S}_2$ .<sup>114</sup> Resinous or asphalt-like substances resulting from sulphurizing paraffin hydrocarbons may be added to rubber before vulcanizing.<sup>115</sup>

Reaction of sulphur monochloride with saturated hydrocarbons yields chlorinated

<sup>107</sup> J. W. leNobel, U. S. P. 1,868,211, July 19, 1932, to Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1932, 26, 5220. See also, P. Sechler, British P. 382,842, 1932, *Chem. Abs.*, 1933, 27, 2030.

<sup>108</sup> R. F. Davis, U. S. P. 1,941,251, Dec. 26, 1933, to Universal Oil Products Co., *Chem. Abs.*, 1934, 28, 1520.

<sup>109</sup> British P. 397,699, 1932, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1933, 929.

<sup>110</sup> N. D. Zelinskii and V. A. Smirnov, *Brennstoff-Chem.*, 1925, 6, 249; *Chem. Abs.*, 1925, 19, 3476.

<sup>111</sup> See also Chapters 58, 59 and 60.

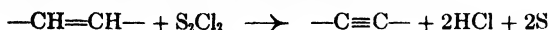
<sup>112</sup> E. Prothière, *Pharm. Ztg.*, 1903, 48, 78; *Chem. Zentr.*, 1903, 1, 1344. H. Gfeller and K. Schaefer, *Schweiz. Apoth. Ztg.*, 1929, 67, 109; *Chem. Abs.*, 1930, 24, 4997. H. Siebeneck, *Petroleum Z.*, 1922, 18, 281; *Chem. Abs.*, 1922, 16, 3200.

<sup>113</sup> W. Friedmann, *Ber.*, 1916, 49, 1344. W. Markownikow and J. Spady, *Ber.*, 1887, 20, 1850. For a discussion of the reactions of hydrocarbons with sulphur, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

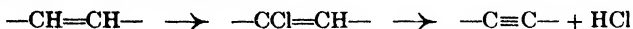
<sup>114</sup> W. Friedmann, *Ber.*, 1916, 49, 1515.

<sup>115</sup> H. Klein and A. Beck, German P. 566,724, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2001.

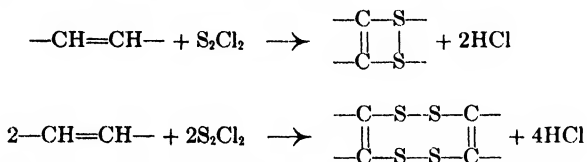
compounds accompanied by the evolution of hydrogen chloride.<sup>116</sup> Simultaneously polymerized substances are formed, probably from unsaturated hydrocarbons due to elimination of hydrogen chloride from the chlorinated compounds. With ethylenic hydrocarbons apparently two hydrogen atoms are removed yielding hydrocarbons containing a triple bond. This may occur in one of two ways: either direct elimination of hydrogen as hydrogen chloride



or substitution of one hydrogen at low temperatures followed by subsequent dechlorination at higher temperatures.



Other possibilities are the formation of cyclic compounds



Asphaltic bodies are made by treating petroleum distillates with sulphur or sulphur monochloride. Thus, Hermes<sup>117</sup> heated a mixture of 11 parts of tar, 2 parts of resin and 1 part of sulphur to the melting point of sulphur and then added 11 parts of powdered lime to the brown, thickened mass. The product was a brown, opaque, resinous mass insoluble in water.

Landsberg<sup>118</sup> obtained an insoluble sulphur-containing material by the action of sulphur and sulphur monochloride on oils from the dry distillation of acid sludge.

Knight<sup>119</sup> secured an extremely hard material by heating residual hydrocarbons (asphaltum, pitch, natural bitumen) with about 1 per cent of sulphur to 204°C. Reducible metallic oxides, such as those of iron, lead or manganese were added to assist dehydrogenation and subsequent hardening. Earthy substances (aluminum silicate, talc, calcium carbonate and silica) also are incorporated. The resulting plastic may be molded into various forms. It is described as non-porous, non-adsorptive and resistant to acid and alkali corrosion. Dehydrogenation of petroleum residues and subsequent condensation of the unsaturated hydrocarbons, by heat and pressure, is recommended by Murez.<sup>120</sup>

Another procedure<sup>121</sup> comprises distilling a mixture of crude oil and calcium carbonate to a temperature of 274°C., the latter being added to neutralize any sulphuric acid formed. The residue is treated at 250°C. with sufficient sulphur to give the desired consistency. Residues from certain Rumanian oils require about 7.4 per cent of sulphur, but too much of this element adversely affects the ductility of the bitumen. Egloff<sup>122</sup> suggests heating residues from cracked distillates with 5-10 per cent of sulphur (or sulphur compounds) at 260°C. and a pressure of 50 pounds for 6 hours. Volatile compounds are continuously removed during the operation.

<sup>116</sup> J. V. Meigs, *Ind. Eng. Chem.*, 1917, 9, 655. E. Lorand, *ibid.*, 1927, 19, 733.

<sup>117</sup> R. Hermes, *British P.* 10,423, 1902; *J.S.C.I.*, 1902, 21, 1326. See also D. W. Peck, *British P.* 24,629 and 24,630, 1898; *J.S.C.I.*, 1899, 18, 1021.

<sup>118</sup> L. Landsberg, *British P.* 8,069, 1913; *Chem. Abs.*, 1914, 8, 3235.

<sup>119</sup> H. Knight, *U. S. P.* 1,505,206, Aug. 19, 1924; *Chem. Abs.*, 1924, 18, 3258.

<sup>120</sup> A. B. Murez, *French P.* 707,745, 1930; *Chem. Abs.*, 1932, 26, 840.

<sup>121</sup> *British P.* 188,854, 1921, to "Bitumul Matita," Soc. Anon. Romana; *J.S.C.I.*, 1923, 42, 46A. C/ A. Montupet, *French P.* 832,772, 1903; *J.S.C.I.*, 1903, 22, 1289.

<sup>122</sup> G. Egloff, *U. S. P.* 1,896,227, Feb. 7, 1933, to Universal Oil Products Co.; *Brit. Chem. Abs. B*, 1933, 929.



## RESINS FROM ACID SLUDGE AND PETROLEUM SULPHONIC ACIDS

Concentrated or fuming sulphuric acid reacts with various types of petroleum hydrocarbons to form oxygenated, condensed or sulphonated products.<sup>123</sup>

Refining of petroleum distillates with sulphuric acid yields large quantities of acid sludge, its formation being at a maximum in the drastic treatment of heavier fractions for white oils and medicinal paraffins. However, even in the less severe treatment of lubricating oils, sludges are formed which tend to become solid. Hydrocarbons responsible for such are not true unsaturates, such as are present in cracked distillates, but are more likely polynuclear naphthenes with unstable groupings or bridge structures.<sup>124</sup>

Acid sludge consists of a mixture of unchanged sulphuric acid, oil, viscous or solid oxygenated and resinous substances and sulphonic acids. Weir, Houghton and Majewski<sup>125</sup> state that flocculation and adsorption of (colloidally?) dissolved bitumens as well as sulphonation and oxidation takes place. True sulphonic acids, of which both oil- and water-soluble types exist, may be extracted from acid treated oils or sludge by caustic soda, and their sodium salts freed of sodium sulphate by further extraction with a solvent, such as ethyl or isopropyl alcohol.

Many attempts have been made to utilize acid sludge in the preparation of resins, asphalts and paint bases. Possibly because of the sulphurous nature of the initial material, no high-grade products have been produced therefrom.<sup>126</sup>

The possibility of employing acid sludge and bases in the manufacture of drying oils, varnishes and lacquers has received some attention. For example, it was proposed to make a paint oil, capable of drying to a varnish-like finish by extracting

<sup>123</sup> Although aromatic hydrocarbons form sulphonic acids almost exclusively, many of the paraffins and naphthenes undergo simultaneous oxidation and sulphonation. R. A. Worstell, *Am. Chem. J.*, 1898, 20, 664; *J.C.S.*, 1899, 76 (1), 18. G. N. Burkhardt, *J.C.S.*, 1930, 2387. C. J. Istrati and M. Michalescu, *Bull. Soc. Sci. Bucharest*, 1904, 13, 143; *Chem. Zentr.*, 1904, 2, 1447. Hydrocarbons containing a tertiary grouping are more readily sulphonated and oxidized than straight chain aliphatics and the large losses experienced in acid refining of mineral lubricating oils may be attributed partly to sulphonation and oxidation of such branched-chain compounds. B. T. Brooks, "The Non-Benzenoid Hydrocarbons," The Chemical Catalog Co., Inc., New York, 1922, 63.

<sup>124</sup> A. E. Dunstan and F. B. Thole, *J. Inst. Pet. Tech.*, 1918, 4, 191.

<sup>125</sup> H. M. Weir, W. F. Houghton and F. M. Majewski, *Ind. Eng. Chem.*, 1930, 22, 1293.

<sup>126</sup> For methods of separating resins from mineral oils, residuum and acid sludge by solvents, see B. Diamond, German P. 173,616 and 176,468, 1904; *J.S.C.I.*, 1907, 26, 87; *Chem. Abs.*, 1907, 1, 1350. C. Daeschner, *Rev. prod. chim.*, 4 (20), 309; *J.S.C.I.*, 1902, 21, 168. British P. 10,663, 1901; *J.S.C.I.*, 1902, 21, 765. L. Singer, British P. 109,270, 1917; *Chem. Abs.*, 1918, 12, 93. An asphalt-like product is obtained by washing acid sludge with gasoline and water to remove oil and sulphuric acid, respectively; L. Landsberg, U. S. P. 1,211,721, Jan. 9, 1917; *Chem. Abs.*, 1917, 11, 1039. An acid resin obtained in refining petroleum, after removal of free sulphuric acid, is dried and agitated at 120-125°C. with concentrated sulphuric acid, German P. 333,169, 1913, to Harburger chem. Werke Schön & Co.; *J.S.C.I.*, 1921, 40, 339A. Acid tar, note, A. G. Wass, British P. 13,885, 1887; *J.S.C.I.*, 1888, 7, 663. Hardening tars, H. Trillich, German P. 200,524, 1907; *J.S.C.I.*, 1908, 27, 974. J. C. Berntrup and M. L. Q. van Leiden Hulzebosch (British P. 8,462, 1898; *J.S.C.I.*, 1899, 18, 361) state that solidification of petroleum residues is effected by intimately rubbing together, for a prolonged time, a mixture of them and resin with slaked lime and water until a tough mass is produced which will harden on standing. This can be molded by pressure into a firm body. Asphalts in petroleum refining, note, C. B. Forward and J. M. Davidson, British P. 20,879, 1896; *J.S.C.I.*, 1899, 18, 128. J. A. Soriano (French P. 332,051, 1903; *J.S.C.I.*, 1903, 22, 1196; 1904, 23, 55) mixed a bitumen composition with an alkali earth compound to convert acid tar from petroleum into a product resembling purified soft bitumen, the tar is kneaded with an amount of iron filings or borings more than sufficient to combine with the sulphuric acid present; C. Rave, British P. 607, 1888; *J.S.C.I.*, 1889, 8, 112; W. P. Thompson, *J.S.C.I.*, 1888, 7, 303. For the production of asphalt from sludge, see M. E. Schmitz, *Bull. soc. ind. Mulhouse*, 1927, 92, 693, 695, 698; *Brit. Chem. Abs.*, B, 1927, 384, 385. Hard pitch from acid sludge: O. Diekmann, U. S. P. 1,703,615, Feb. 26, 1929; *Brit. Chem. Abs.* B, 1929, 466. Oxidizing petroleum residues, see G. H. Grey, British P. 18,302, 1898; *J.S.C.I.*, 1898, 17, 1137. A. V. Adiasewitch (*Zap. imp. russk. tech. obschch.* 29, 93; *J.S.C.I.*, 1896, 15, 346) prepared resinous material from lubricating oil residuum by blowing with "de-oxygenated" air at 150-200°C and subjecting the material to a simultaneous discharge of electricity. See also Kouindjy, *Bull. de la soc. d'encouragement pour l'industrie nationale*, 94, 1116; *J.S.C.I.*, 1896, 15, 533. C. J. Burkley (U. S. P. 1,306,520, June 10, 1919; *Chem. Abs.*, 1919, 13, 2140) subjects a mixture of gilsonite, 5 parts, and cylinder oil, 6 parts, to air blowing at 175-225°C. for about 3 hours and produces a tough plastic material with a dull luster. W. Daitz (German P. 336,603, 1918, to Harburger chem. Werke Schön & Co.; *J.S.C.I.*, 1921, 40, 651A) makes a hard asphalt from residues, obtained in treatment of mineral oils, by mixing with magnesium oxide and water (to neutralize free acid) and then blowing with air at 130-170°C. See also W. R. Wardell, U. S. P. 1,385,511, July 26, 1921, to Central Commercial Co.; *J.S.C.I.*, 1922, 41, 5A.

sludge with water, neutralizing the oily or resinous residue and removing the separated oil.<sup>127</sup> Or the neutralized residue was dissolved in a mixture of alcohol and benzene, oil of turpentine or tar oil to give a lacquer.<sup>128</sup> The latter was said to be quick drying, owing to the presumed siccative properties of the petroleum acids, and could be used on wood, metal and leather.

Bird<sup>129</sup> suggests diluting sludge with water to approximately 25 per cent concentration, warming to about 100°C., and treating with a halogenating agent, e.g., sodium chlorate. The resinous body thus formed, when hot, is a translucent mass and can be drawn into long silky threads possessing a coppery luster. On cooling it becomes friable and can be ground to a powder. The resin dissolves in alcohol and evaporation of the solvent yields reddish-brown scales similar in appearance to shellac. This substance may be employed in the manufacture of phonograph records, insulating media and as a constituent of moldings.

Preparation of resins from oil-refining sludges is described by Demann.<sup>130</sup> Three methods are advanced which consist of treatment (a) with bleaching earths, such as silica gel or fuller's earth; (b) with substances which coagulate or resinify, e.g., phenols, sodium phenolate or formaldehyde; or (c) with water and a heavy benzine, benzene, tetralin, or liquids of either a strongly aliphatic or polymethylene character. Products are separated from the acid or other associated liquids.

Substances resembling blown asphalts are obtained by the following procedure.<sup>131</sup> Approximately equal quantities of petroleum asphalt and sludge are heated to 120°C. After thorough agitation, the temperature is raised slowly to 250°C. and maintained until complete decomposition of acid compounds is effected. A mixture of petroleum residues and animal or vegetable oils may be subjected in like manner to the action of sulphuric acid at 120°. After removal of volatile components, by distillation, a plastic or elastic residuum is obtained.<sup>132</sup>

Water-soluble petroleum sulphonic acids, or "green" acids, are extracted from acid sludge with alkalis.<sup>133</sup> These substances are readily soluble in alcohols, chloroform and benzene, and less soluble in carbon tetrachloride, carbon disulphide, ether, naphtha and xylene. They appear to be monosulphonic acids having molecular weights of about 400-500. When anhydrous, the acids are dark, gummy hygroscopic materials or even solids and somewhat resinous.

Oil-soluble, or "mahogany," sulphonic acids are secured by washing acid treated and neutralized high-boiling petroleum distillates with solvents such as an aqueous solution of acetic acid or its water-soluble esters,<sup>134</sup> or with isopropyl alcohol.<sup>135</sup> Such acids are lighter in color than green acids, and are soluble in ether or chloroform but insoluble in amyl alcohol.

According to von Pilat, Sereda and Szankowski,<sup>136</sup> three classes of petroleum sulphonic acids may be distinguished by the solubility of their calcium salts:

<sup>127</sup> Millochan, U. S. P. 37,918, Mar. 17, 1863. G. W. J. Bradley (British P. 412,343, 1934, to Woodall-Duckham, Ltd.; *Chem. Abs.*, 1934, 28, 7564) suggests treating acid sludge with boiling water.

<sup>128</sup> R. Zalosiecki, *Chem. Rev. Fett- und Harzindustrie*, 1898, 5 (2), 27; *J.S.C.I.*, 1898, 17, 340.

<sup>129</sup> J. C. Bird, U. S. P. 1,917,869, July 11, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 4666.

<sup>130</sup> W. Demann, British P. 258,241, 1925; *Chem. Abs.*, 1927, 21, 3126. German P. 436,242, 1925; *Brit. Chem. Abs. B*, 1927, 436.

<sup>131</sup> F. R. Moxer and J. Greutert, U. S. P. 1,862,060, June 7, 1932, to Shell Development Co.; *Brit. Chem. Abs. B*, 1933, 538. Cf. L. Bolgar, British P. 227, 291, 1927; *Brit. Chem. Abs. B*, 1928, 252. Hungarian P. 104,822, 1928; *Chem. Abs.*, 1933, 27, 2001.

<sup>132</sup> L. d'Antal, British P. 406,293, 1932; *Brit. Chem. Abs. B*, 1934, 490.

<sup>133</sup> Various methods for obtaining petroleum sulphonic acids are described by Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

<sup>134</sup> P. I. Schestakoff, U. S. P. 1,706,940, Mar. 26, 1929; *Chem. Abs.*, 1929, 23, 2290. British P. 247,940, 1925; *Chem. Abs.*, 1927, 21, 593.

<sup>135</sup> C. I. Robinson, U. S. P. 1,387,868, Aug. 16, 1921, to Standard Oil Development Co.; *Chem. Abs.*, 1921, 15, 4048. E. B. Cobb, U. S. P. 1,387,835, Aug. 16, 1921, to Standard Oil Development Co.; *J.S.C.I.*, 1921, 40, 728A. E. B. Cobb and A. Holmes, U. S. P. 1,707,187, Mar. 26, 1929, to Standard Oil Development Co.; *Brit. Chem. Abs. B*, 1929, 634.

<sup>136</sup> S. von Pilat, J. Sereda and W. Szankowski, *Petroleum Z.*, 1933, 29, 1; *Brit. Chem. Abs. B*, 1933, 211. S. von Pilat and E. Davidson, *Petroleum Z.*, 1923, 24, 1559; *Brit. Chem. Abs. B*, 1929, 47.

$\alpha$ -Sulphonic acids occurring principally in acid sludge, but also partly in the oil layer; the calcium salts are soluble in water or ether.

$\beta$ -Sulphonic acids; found mainly in the oil phase but also in sludge when oleum is used; the calcium salts are insoluble in water but soluble in ether.

$\gamma$ -Sulphonic acids; present only in acid sludge; the calcium salts are soluble in water but insoluble in ether.

Salts of both green acids and mahogany acids have been suggested as constituents of lubricants. Such a material to be used in the die-drawing of metals consists of sodium salts of water-soluble acids, tallow and water, the ingredients being heated to 82°C. to effect homogeneous mixing.<sup>137</sup> Alkali salts of oil-soluble acids, either alone<sup>138</sup> or emulsified with mineral oils and animal fats,<sup>139</sup> have been proposed also. Another preparation contains petroleum lubricating oil, an alkali soap of a fatty acid (e.g., sodium oleate) and an alkali metal oil-soluble sulphonate.<sup>140</sup> The latter facilitates feeding of the lubricant by a wick. A similar mixture may be employed for lubricating artificial silk during spinning.<sup>141</sup>

A flexible, transparent, gelatinous product is made by evaporation of an aqueous solution of gelatin containing a clear oil (medicinal white oil) emulsified with the aid of mahogany sulphonates.<sup>142</sup>

Heavy metal sulphonates may be used as driers, either alone or in combination with other driers.<sup>143</sup> For example, sodium salts of oil-soluble sulphonates, after extraction with 35-65 per cent aqueous alcohol, are freed of oil with 10-20 per cent of gasoline. The salts then are converted to oil-soluble lead, cobalt or manganese sulphonates, and the latter separated from insoluble material with an organic solvent, e.g., a mixture of benzene containing 75 per cent of ethyl or isopropyl alcohol. A composition of 5-25 per cent of oil-soluble calcium sulphonates, 5-25 per cent resins and 50-90 per cent of a drying oil is suggested as the film-forming constituent of varnishes.<sup>144</sup>

#### RESINS FROM CHLORINATED PETROLEUM HYDROCARBONS

Chlorination of petroleum hydrocarbons has been utilized in two distinct ways for producing synthetic resins. In some cases the chlorinated derivatives of high-boiling petroleum fractions are resins or resin substitutes. In other instances elimination of hydrogen chloride from such chlorinated material yields hydrocarbons of varying degrees of unsaturation, some of which may be polymerized to resinous substitutes or used as drying oil substitutes.

#### CHLORINATED PETROLEUM HYDROCARBONS<sup>145</sup>

Paraffin, ceresin, montan wax and petroleum oil can be chlorinated to a high degree by dissolving in carbon tetrachloride and introducing chlorine for a pro-

<sup>137</sup> H. L. Johnson, U. S. P. 1,795,491, Mar. 10, 1931, to Standard Oil Development Co.; *Brit. Chem. Abs.*, B, 1931, 1039.

<sup>138</sup> J. C. Sharp, U. S. P. 1,789,054, Jan. 13, 1931, to Standard Oil Co. of Ind.; *Brit. Chem. Abs.*, B, 1931, 847.

<sup>139</sup> E. W. Adams, U. S. P. 1,871,939 and 1,871,940, Aug. 16, 1932, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1932, 26, 6119, 6160. M. H. Arveson, U. S. P. 1,871,941 and 1,871,942, Aug. 16, 1932, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1932, 26, 6119.

<sup>140</sup> A. E. Becker, U. S. P. 1,888,794, Nov. 29, 1932, to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 1745.

<sup>141</sup> A. E. Becker and de V. Stonaker, British P. 277,637, 1927, to Standard Oil Development Co.; *Brit. Chem. Abs.*, B, 1929, 202.

<sup>142</sup> H. Heckel, U. S. P. 1,902,304, Mar. 21, 1933, to Twitchell Process Co.; *Brit. Chem. Abs.*, B, 1933, 1023.

<sup>143</sup> H. Buc, U. S. P. 1,686,484, 1,686,485, 1,686,486, Oct. 2, 1928, to Standard Oil Development Co.; *Brit. Chem. Abs.*, B, 1929, 530.

<sup>144</sup> H. Buc, U. S. P. 1,735,493, Nov. 12, 1929, to Standard Oil Development Co.; *Chem. Abs.*, 1930, 24, 739.

<sup>145</sup> A more extensive discussion of resins from chlorinated hydrocarbons is given in Chapter 56.

tracted period. If a rise in temperature occurs during the early stages of the reaction, the temperature is allowed to fall before introduction of chlorine is continued. In this way paraffin, containing 70 per cent of chlorine, furnishes a transparent solid substance. Highly chlorinated paraffin is very resistant to acids and alkalis. It is not attacked by boiling 65 per cent nitric acid, concentrated hydrochloric acid or 10 per cent aqueous caustic soda solution. Chlorinated ozokerite is scarcely effected by fuming nitric acid at 300°C. under pressure. In spite of this resistance to various reagents, chlorinated aliphatics exhibit a tendency to split off hydrogen chloride on long standing. Apparently the chlorine atoms are not bound so firmly as in chloronaphthalenes (Halowax).<sup>146</sup> The use of various chlorinated paraffins in the manufacture of chewing gum is described by Geller.<sup>147</sup>

Chlorination products of drying oils, paraffin wax, naphthalene and various other substances are employed by Blakeman<sup>148</sup> in paints. Asphaltic oils, fish oil, waxes and coal-tar, all chlorinated to a greater or lesser degree, are proposed by Ellis<sup>149</sup> as flame-proof insulators. A mixture of chlorinated asphaltum and chlorinated vegetable oils, the latter serving as a toughening agent, is used by Wickenden<sup>150</sup> in paints and varnishes. For example, petroleum pitch or asphaltum, melting at 120°C., and 10-20 per cent of cottonseed oil are treated with chlorine in carbon tetrachloride solution until absorption is complete. The solvent is removed subsequently by distillation.

#### CHLORINATION AND DECHLORINATION

Methylcyclopentane has been utilized in the preparation of resinous condensation products similar to those from cyclohexadiene.<sup>151</sup> A petroleum fraction (from Caucasian petroleum) boiling from 68-73°C. is chlorinated to yield a dichloromethylcyclopentane. The latter is dissolved in glacial acetic acid and treated with a small proportion of sulphuric acid. Elimination of hydrogen chloride and subsequent polymerization of the resulting methylcyclopentadiene probably occurs. When the dichloro derivative is dissolved in two parts of acetic acid and boiled with 20 per cent of zinc chloride, hydrogen chloride is evolved copiously and a resin precipitated.

Bielouss<sup>152</sup> and Gardner<sup>153</sup> chlorinate petroleum and then dechlorinate the product by heating to 220-240°C. to obtain a drying oil.<sup>154</sup> If the temperature during dechlorination rises above 250°C. resinous and asphaltic substances are formed. Dechlorination is accelerated by catalysts such as metallic iron, aluminum or zinc or their oxides.

Dechlorination may be effected in the presence of rosin, in which case the acidic component (rosin) is neutralized during heating.<sup>155</sup> The resulting product can be used as a paint vehicle. If a high-boiling glyceride, e.g., soya oil or hydro-

<sup>146</sup> German P. 248,779 and 256,856, 1910, and 285,156, 1911, to C. F. Boehringer & Söhne; *J.S.C.I.*, 1912, 31, 886; 1913, 32, 499, 613. French P. 469,261, 1912; *J.S.C.I.*, 1913, 32, 1120.

<sup>147</sup> L. W. Geller, U. S. P. 1,855,016 and 1,855,017, Apr. 19, 1932, to American Chicle Co.; *Chem. Abs.*, 1932, 26, 3346.

<sup>148</sup> W. N. Blakeman, U. S. P. 989,225, 989,226 and 989,227, Apr. 11, 1911; *Chem. Abs.*, 1911, 5, 2190.

<sup>149</sup> Carleton Ellis, U. S. P. 1,246,809 and 1,246,810, Nov. 13, 1917, and 1,248,638, Dec. 4, 1917; *Chem. Abs.*, 1918, 12, 298, 412.

<sup>150</sup> L. Wickenden, U. S. P. 1,398,084, Nov. 22, 1921; *Chem. Abs.*, 1922, 16, 842.

<sup>151</sup> German P. 263,159, 1912, to Badische Anilin- & Soda-Fabrik; *Chem. Abs.*, 1914, 8, 266. British P. 23,543, 1912; *J.S.C.I.*, 1913, 32, 876.

<sup>152</sup> E. Bielouss, U. S. P. 1,384,423, July 12, 1921, to H. A. Gardner; *Chem. Abs.*, 1921, 15, 3758.

<sup>153</sup> E. Bielouss and H. A. Gardner, U. S. P. 1,384,447, July 12, 1921, to H. A. Gardner; *Chem. Abs.*, 1921, 15, 3758.

<sup>154</sup> V. Kiselev (*Masloboino-Zhironoe Delo*, 1932, (8), 26; *Chem. Abs.*, 1933, 27, 3348) states none of the synthetic substitutes for linseed oil is satisfactory and new synthetic products, most likely from naphtha, will have to be developed to replace linseed or wood oil economically. A. Ya. Drinberg and E. M. Prik (*Lakokrasochnaya Ind.*, 1933, 4696, 15; *Chem. Abs.*, 1933, 27, 5202) indicate the possibility of preparing drying oils by chlorinating polymers obtained in petroleum distillation and condensing them with soaps. See also A. Ya. Drinberg, *J. Appl. Chem. Russ.*, 1934, 7, 1046, 1206; *Brit. Chem. Abs. B*, 1935, 818.

<sup>155</sup> H. A. Gardner, U. S. P. 1,412,399, April 11, 1922; *Chem. Abs.*, 1922, 16, 2233.

generated whale oil, be substituted for rosin and the mixture distilled under reduced pressure, then a distillate is obtained which possesses the properties of a drying oil and the residue (after cooling) is generally a hard, brittle resin.<sup>108</sup> The latter may be employed in varnishes. Unsaturated, or dechlorinated, oils can be compounded with rubber and utilized in the manufacture of molded articles or rubberized fabrics.<sup>107</sup>

Viscid resinous condensation products are made from high-molecular-weight hydrocarbons by successive halogenation and dehalogenation followed by evaporation, or from heavy petroleum oils by chlorination and subsequent treatment with Devarda's alloy.<sup>108</sup> On distillation, the resinous products give a residue of pitch which is said to be applicable as a brewer's pitch.<sup>109</sup> The distillate can be submitted again to the same treatment. Oil-like bodies, recovered from petroleum tar by distillation under reduced pressure, are converted into non-reactive resins by chlorination followed by distillation.<sup>100</sup> Extraction of the distillation residue with a selective solvent yields the purified resin.

The following procedure is suggested by Hultman<sup>101</sup> for preparing a soft, rubbery, vulcanizable material. A mineral oil boiling above 205°C. is treated at temperatures below its boiling point with a polymerizing agent, e.g., cerium oxide or dioxide. The product is cooled to about 17°C. and subjected to the action of an activated reducing gas (such as methane and carbon monoxide contacted with nickel or platinum at 205°C.) and finally to a halogenating agent, chlorine, bromine or boron fluoride. The rubbery product can be readily separated from the bulk of the oily mass.

Morrell and Egloff<sup>102</sup> described the chlorination of polymerized hydrocarbons, obtained from petroleum distillates, in the presence of phenols. The viscosity of the product is regulated by the proportion of chlorine employed.

Hydrocarbons resulting from the destructive hydrogenation of oil or coal are subjected to the action of dehydrogenating agents, e.g., chromic oxide at 500°C. The product is treated with aqueous hydrochloric acid and then passed over barium chloride. The resulting olefins are reacted with chlorine and again dechlorinated, by elimination of hydrogen chloride. Polymerization with sodium of the unsaturated hydrocarbon thus formed gives resinous or rubber-like bodies.<sup>103</sup>

#### RESINS FROM CRACKED DISTILLATES

Hydrocarbon oils, which have been subjected to thermal decomposition, or cracking, differ in important respects from corresponding fractions from crude petroleum. Unlike crude mineral oils, cracked products contain unsaturated hydrocarbons including monolefins, diolefins and olefins having aromatic substituents.<sup>104</sup> The proportion of unsaturated hydrocarbons in, for example, a cracked gasoline

<sup>100</sup> H. A. Gardner, U. S. P. 1,463,834, Apr. 7, 1923, and 1,484,018, Feb. 2, 1924; *Chem. Abs.*, 1923, 17, 3260; 1924, 18, 1194.

<sup>107</sup> H. A. Gardner, U. S. P. 1,446,039, Feb. 20, 1923; *Chem. Abs.*, 1923, 17, 1560.

<sup>108</sup> Devarda's alloy is an alloy of aluminum containing varying proportions of copper and zinc. A typical composition is 59 parts of aluminum, 39 parts of copper and 2 parts of zinc.

<sup>109</sup> H. Rebs, German P. 343,466, Aug. 7, 1915; *J.S.C.I.*, 1922, 41, 110A.

<sup>100</sup> S. C. Fulton, U. S. P. 1,931,824, Nov. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, 29, 589. British P. 397,699, 1932; *Brit. Chem. Abs. B*, 1933, 929. French P. 744,169, 1933; *Chem. Abs.*, 1933, 27, 4109.

<sup>101</sup> E. W. Hultman, U. S. P. 1,704,194, Mar. 5, 1929, to F. P. Dunklee, J. Monteleone and W. R. Simons; *Brit. Chem. Abs. B*, 1929, 368.

<sup>102</sup> J. C. Morrell and G. Egloff, U. S. P. 1,744,135, Jan. 21, 1930, to Universal Oil Products Co., *Brit. Chem. Abs. B*, 1930, 997.

<sup>103</sup> C. Krauch and M. Müller-Conradi, U. S. P. 1,823,495, Sept. 15, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 291.

<sup>104</sup> A proposed method of purifying used lubricating oils involves reducing them with a hyposulphite. A. Franke and G. Thomas, French P. 768,179, 1934; *Chem. Abs.*, 1935, 29, 594.

depends mainly upon the temperature and duration of cracking, and the pressure.<sup>166</sup> High temperature (about 600°C.) cracking at approximately atmospheric pressure, so-called vapor-phase processes, yields gasoline with a relatively large proportion of olefins. At lower temperatures and superatmospheric pressures, sometimes designated liquid-phase cracking, distillates with a smaller percentage of unsaturates are produced.

Cracked distillates, especially cracked gasoline, because of these unsaturated hydrocarbons may be regarded as a potential source of synthetic resins. Resinous or gummy substances obtained by oxidation of such hydrocarbons, particularly by exposure of cracked gasoline to air or oxygen, though as yet of no practical value are discussed because they appear to have some possibilities. Perhaps the most successful method of utilizing olefins in cracked distillates as raw materials for resins is by controlled polymerization. An example of such a procedure is the action of aluminum chloride on gasolines containing monoolefins, diolefins and aromatics. Of interest in this connection is the formation of resinous products in the large-scale refining of cracked gasoline with sulphuric acid, zinc chloride or activated earths.

**Gumming of Cracked Gasolines.** When cracked gasolines are allowed to stand in contact with air for prolonged periods of time a semi-fluid, brown, sticky mass gradually accumulates in the container. This material is designated "gum" because of its similarity in appearance and consistency to natural gums. Its formation is accelerated by bright sunlight or rise in temperature. Gum is produced also by evaporation of cracked gasolines in the presence of air.

The formation of gummy deposits, by slow oxidation of oils, was probably noted first by Schönbein.<sup>166</sup> Such resinification is described also by Hall<sup>167</sup> and by Dunstan and Pitkethly<sup>168</sup> for cracked distillates, by Nash<sup>169</sup> for oils separated from Athabaska "oil sands," by Hoffert and Claxton for crude benzol,<sup>170</sup> and by Forbes-Leslie<sup>171</sup> and Neubronner<sup>172</sup> for shale oil distillates. A study of these resins from the standpoint of petroleum refining was made by Ellis and Wells.<sup>173</sup> Procedures for removal of resin-forming hydrocarbons from petroleum distillates are discussed by Petrov,<sup>174</sup> Schwartz,<sup>175</sup> Black and Chappell,<sup>176</sup> Teplitz,<sup>177</sup> and others.<sup>178</sup>

The work of Smith and Cooke<sup>179</sup> indicated oxidation of hydrocarbons to aldehydes and polymerization of the latter to be the cause of gum- and resin-formation in cracked gasolines. Moisture and light accelerated these reactions. At first

<sup>166</sup> For a discussion of the effects of these factors on the composition of cracked gasoline, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

<sup>167</sup> Schönbein, *J. prakt. Chem.*, 1866, (1) 98, 257; 1867, (1) 100, 496, 1867, (1) 201, 145. See also C. Engler and H. v. Hofer, "Das Erdöl," S. Hirzel, Leipzig, 1913, 1, 517.

<sup>168</sup> W. A. Hall, *J. Inst. Pet. Tech.*, 1915, 1, 147.

<sup>169</sup> A. E. Dunstan and R. Pitkethly, *Ind. Eng. Chem.*, 1929, 21, 643.

<sup>170</sup> A. W. Nash, *J. Inst. Pet. Tech.*, 1927, 13, 681.

<sup>171</sup> W. H. Hoffert and G. Claxton, *J.S.C.I.*, 1933, 52, 25T.

<sup>172</sup> W. Forbes-Leslie, *J.S.C.I.*, 1924, 43, 537T.

<sup>173</sup> K. Neubronner, *Petroleum Z.*, 1927, 23, 789; *Brit. Chem. Abs. B.*, 1927, 737.

<sup>174</sup> Carleton Ellis and A. A. Wells, *Ind. Eng. Chem.*, 1915, 7, 1029. Note also Carleton Ellis, U. S. P. 1,328,060 and 1,321,061, Oct. 7, 1919, to Ellis-Foster Co.; *J.S.C.I.*, 1919, 38, 891A.

<sup>175</sup> G. Petrov, *British P.* 291,823, 1927; *Chem. Abs.*, 1929, 23, 1260.

<sup>176</sup> F. Schwartz, *Petroleum Z.*, 1928, 24, 803; *Brit. Chem. Abs. B.*, 1928, 591.

<sup>177</sup> J. C. Black and M. L. Chappell, U. S. P. 1,810,068, June 16, 1931; *Chem. Abs.*, 1931, 25, 4697.

<sup>178</sup> M. Teplitz, U. S. P. 1,801,213, March 14, 1931, to Corona Conversion Corp.; *Brit. Chem. Abs. B.*, 1932, 10.

<sup>179</sup> For a review of methods of removing gum-forming constituents by refining or prevention of gum by addition of inhibitors, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934. V. A. Kalichevsky and B. A. Stagner, "Chemical Refining of Petroleum," The Chemical Catalog Co., Inc., New York, 1933. A discussion of the resinification of gasoline is given by E. Norlin, *Tek Tid, Uppl. C, Kemi*, 1933, 63, 89; *Chem. Abs.*, 1934, 28, 1849. F. Sager (*J. Inst. Pet. Tech.*, 1934, 20, 1044) reports the isolation of a naturally occurring inhibitor (probably p-cresol) from cracked Rumanian gasoline. For a study of the effect of various inhibitors on cracked gasoline, see C. G. Dryer, J. C. Morrell, G. Egloff and C. D. Sowry, *Ind. Eng. Chem.*, 1935, 27, 15.

<sup>180</sup> N. A. C. Smith and M. B. Cooke, *Bureau of Mines, Reports of Investigations*, 1922, 2394; *Chem. Abs.*, 1922, 16, 4332.

it was thought that phenol-aldehyde resins were formed, but the absence of phenols and further investigations on the behavior of aldehydes led Smith and Cooke to the conclusion that aldehydes alone were responsible for resinification. It was noted that gum initially obtained was sticky, but on standing became harder, and on prolonged drying ultimately gave a hard, brittle resin. The latter was partly soluble in acetone, whereas soft gum was entirely soluble in that solvent. As much as 18 per cent of oxygen was present in some gums.

Brooks<sup>190</sup> studied the gum obtained by slow oxidation of cracked gasoline and found it contained a complex mixture of organic peroxides, aldehydes, ketones and acids. He also showed that aldehydes alone were not capable of forming gum under his experimental conditions. However, Wagner and Hyman<sup>191</sup> noted that a solution of crotonaldehyde in straight-run gasoline, subjected to the action of oxygen and light, yielded considerable quantities of gum similar in characteristics to that from cracked gasoline.

As a result of his work, Brooks put forward the theory that the initial step in gum-formation consisted in the development of organic peroxides, of the type



acids were regarded as decomposition and reaction products of the peroxides. In support of this view, Brooks found that a marked positive test for peroxides can be obtained in a refined cracked gasoline after exposure to air and sunlight for half an hour. Furthermore, freshly-formed gums contained a substantial proportion of explosive organic peroxides. This theory of the intermediate formation of peroxides has been substantiated by other investigators. The unsaturated compounds responsible for the production of peroxides are probably conjugated diolefins, aromatic olefins and similar reactive unsaturated hydrocarbons.<sup>192</sup>

Tauss<sup>193</sup> concluded that the color which appears when benzenes or benzols are shaken with sulphuric acid is the result of a condensation of sulphur or oxygen compounds with olefins. When exposed to air the dye, thus formed, goes over to acid resins. Carpenter<sup>194</sup> states color reversion is due to unstable resin-forming bodies, some of which are members of the cyclopentadiene family, including indene, cumarone, fulvenes, fluorene and their homologues. Hydrocarbons of these classes exhibit a strong tendency towards peroxide formation. Amend<sup>195</sup> observed the presence of a small proportion of terpenes, and related hydrocarbons, in cracked distillates. Such hydrocarbons were easily converted by oxygen into resinous or rubber-like bodies. Baxter<sup>196</sup> noted that oxygen was necessary for gum-formation in gasolines from Colorado oil shales. Reaction was more rapid in sunlight than in the dark and was accelerated also by ozone but inhibited by phenylhydrazine. Gums from shale gasoline were soluble in methyl alcohol.

Cassar<sup>197</sup> reports that simple monolefins, when added to olefin-free gasoline in

<sup>190</sup> B. T. Brooks, *Ind. Eng. Chem.*, 1926, 18, 1198.

<sup>191</sup> C. R. Wagner and J. Hyman, *J. Inst. Pet. Tech.*, 1929, 15, 674 *Amer. Pet. Inst., Proc. Ann. Meeting*, 1930, 11 (1, Sect. 3), 118; *Chem. Abs.*, 1930, 24, 2282.

<sup>192</sup> For the formation and reactions of peroxides see C. Engler, *Ber.*, 1900, 33, 10 0, 1097. A. Bach, *Compt. rend.*, 1897, 124, 951; *J. C. S.*, 1897, 72 (2), 401. C. Engler and W. Wild, *Ber.*, 1897, 30, 1669. C. Engler and W. Frankenstein, *Ber.*, 1901, 34, 2933. H. Staudinger, *Ber.*, 1925, 58, 1075. W. P. Jorissen and P. A. A. van der Brek, *Rec. trav. chim.*, 1926, 45, 245; *Chem. Abs.*, 1926, 20, 2322. H. N. Stephens, *J. A. C. S.*, 1928, 50, 568. C. Moureu and C. Dufraisse, *Bull. soc. chim.*, 1924, 35, 1564; *Chem. Abs.*, 1925, 19, 1126. S. F. Birch and R. Stansfield, *Nature*, 1929, 123, 490. *Chem. Abs.*, 1929, 23, 2813. J. A. C. Yule and C. P. Wilson, *Ind. Eng. Chem.*, 1931, 23, 1254. P. N. Kogerman, *Trans. 2nd World Power Conf., Berlin*, 1930, 8, 33; *Chem. Abs.*, 1931, 25, 5549. C. G. Dryer, C. D. Sowry, J. C. Morrell and C. Egloff, *Ind. Eng. Chem.*, 1924, 26, 885.

<sup>193</sup> J. Tauss, *Z. angew. Chem.*, 1928, 41, 628.

<sup>194</sup> J. A. Carpenter, *J. Inst. Pet. Tech.*, 1926, 12, 518. See also, G. A. Burrell, *Ind. Eng. Chem.*, 1928, 20, 602.

<sup>195</sup> O. P. Amend, U. S. P. 1,423,064, July 18, 1922; *J. S. C. I.*, 1923, 42, 760A.

<sup>196</sup> R. A. Baxter, *Ind. Eng. Chem.*, 1929, 21, 1096.

<sup>197</sup> H. A. Cassar, *Ind. Eng. Chem.*, 1931, 23, 1132.

concentrations as high as 20 per cent, do not yield gum even when subjected at 100°C. to air under 100 pounds pressure. Diolefins in gasoline, however, readily form gum on evaporation of the solvent. Aliphatic or cyclic diolefins and monolefins attached to a benzene ring are considered the gum-forming constituents of gasoline by Flood, Hladky and Edgar.<sup>122</sup> Fractions of cracked distillates giving the greatest proportions of gum possessed boiling points corresponding to those of conjugated diolefins and cyclo-olefins.<sup>123</sup> The latter types of hydrocarbons may be removed by treatment of cracked distillates with sulphuric acid or maleic anhydride.<sup>120</sup>

The work of Mardles and Moss<sup>121</sup> also indicates that gumming of cracked spirits is essentially oxidation involving formation of organic peroxides. Usually on exposure of such liquids to air, there is a period of induction when the rate of gumming is small; this is followed by more rapid reaction as the products of oxidation accumulate. The rate is increased also by (1) aeration, (2) increased temperatures, (3) action of actinic light, and (4) the presence of certain sulphur and easily peroxidizable compounds. On the other hand, gumming is inhibited by addition of "anti-oxygen," e.g., phenol or thymol, by surfaces, such as soda-lime, iron or copper gauze,<sup>122</sup> and by water. A light-colored viscous gum was prepared by heating vapor-phase gasoline at 50°C. for about three weeks. Steam distillation of the gum yielded organic acids, aldehydes and other oxygenated hydrocarbons, and neutral oil. Furthermore, this gum, which also contained active oxygen, was soluble in hot water to the extent of about 30 per cent, and the remainder dissolved in dilute caustic soda solution. These results are comparable with those obtained by Brooks with a pale yellow resin which had been stored for about 6 months. This resin contained 30 per cent of material soluble in water, 30 per cent of neutral oil consisting chiefly of aldehydes and ketones, and about 40 per cent soluble in 3 per cent aqueous alkali. On distilling the gummy residue from cracked gasoline, Wagner and Hyman<sup>124</sup> observed a series of explosions and the evolution of vapors of acrolein. Similar observations on the decomposition of residues from cracked distillates were previously reported by Ellis and Wells.<sup>124</sup>

An examination of resins made from cracked gasolines under various conditions is reported by Story, Provine and Bennett.<sup>125</sup> That obtained by evaporation of the gasoline in a copper dish was a brown powder, insoluble in water and almost completely insoluble in acetone, alcohol or chloroform. It had a molecular weight of 200, began to soften at 98°C., melted at 105°C. and boiled with decomposition at 164-169°C. On heating with alcoholic potassium hydroxide, a large proportion of the material was saponified. One hundred grams of the gum, under the latter conditions, yielded only 13 g. of unsaponifiable constituents, while 55.0 g. of water-insoluble and 30.5 g. of water-soluble acids were recovered from the hydrolyzed product.

Exposure of cracked gasoline to sunlight and air at 27°C. gave a gum which was a viscous, sticky liquid, and gradually turned brown. When dried, this

<sup>122</sup> D. T. Flood, J. W. Hladky and G. Edgar, *Ind. Eng. Chem.*, 1933, 25, 1234.

<sup>123</sup> S. M. Martin, W. A. Gruse and A. Lowy, *Ind. Eng. Chem.*, 1933, 25, 381.

<sup>120</sup> Reaction between maleic anhydride and conjugated diolefins is discussed in Chapter 40.

<sup>121</sup> E. W. J. Mardles and H. Moss, *J. Inst. Pet. Tech.*, 1929, 15, 657.

<sup>122</sup> On the other hand, the "copper-dish method" for determination of gum usually yields higher and more erratic results than methods employing other surfaces, e.g., glass or porcelain. This may be attributed possibly to the catalytic effect of copper. See, for example, V. Voorhees and J. O. Eisenger, *Oil and Gas J.*, 1928, 27 (31), 152; *Chem. Abs.*, 1929, 21, 2286. W. Littlejohn, W. H. Thomas and H. B. Thompson, *J. Inst. Pet. Tech.*, 1930, 16, 684. E. B. Hunn, H. G. M. Fischer and A. J. Blackwood, *S. A. E. Journal (Penn. Sect. Paper)*, 1930, 26, 31; *Nat. Pet. News*, 1929, 21 (43), 65; *Chem. Abs.*, 1930, 24, 2280. M. T. Zamfirescu, *An. Minelor Romania*, 1932, 15, 177; *Brit. Chem. Abs. B*, 1934, 132.

<sup>124</sup> C. R. Wagner and J. Hyman, *J. Inst. Pet. Tech.*, 1929, 15, 676.

<sup>124</sup> Carleton Ellis and A. A. Wells, *Ind. Eng. Chem.*, 1915, 7, 1029.

<sup>125</sup> L. G. Story, R. W. Provine and H. T. Bennett, *Ind. Eng. Chem.*, 1929, 21, 1079.



soft gum was converted into a material very similar to that produced by the copper dish method. The dried gum had a molecular weight of 338 and on saponification with alcoholic potassium hydroxide yielded the following substances:

	Per Cent
Unsapönifiable matter { Steam-volatile . . . . .	12 20
{ Non-volatile . . . . .	8 93
Steam-volatile acids . . . . .	6 20
Non-volatile acids { Water-insoluble . . . . .	38 24
{ Water-soluble . . . . .	33 18

All gums were the result of oxidation reactions and peroxides were present in the early stages. The chief constituents were acids which, from their physical properties and composition, appeared to be polymers of unsaturated acids. Absence of saturated fatty acids is significant. The unsapönifiable portion resembled polymerized aldehydes, ketones and oxides. Gum formed in sunlight differed from that obtained by evaporation in being more highly polymerized or condensed and also more extensively oxidized.

It is interesting to note that gums are formed by the action of phosphorus pentoxide at 30-50°C. on the unsaturated hydrocarbons in lubricating oils or kerosene.<sup>196</sup> The products are thick, sticky, reddish-brown materials and may be removed from the oil by washing with water.

Wagner and Hyman<sup>197</sup> report that on treating a gasoline, which gave a large proportion of gum on evaporation, with a concentrated solution of alcoholic potassium hydroxide a violent reaction took place accompanied by the formation of a reddish-brown resin.

#### RESINS BY POLYMERIZATION OF CRACKED DISTILLATES

An account of the polymerization of unsaturated hydrocarbons under the influence of heat, energy activation and catalysts is given in Chapter 9. Polymerization of simple monolefins does not yield resinous polymers of high molecular weight, the products being mostly oily or viscous liquids. On the other hand, controlled polymerization of conjugated diolefins and olefins of the styrene type furnishes high-molecular-weight resinous polymers. The use of particular fractions of cracked gasoline as raw materials for such resinous polymerized bodies has been suggested repeatedly.

Reference has been made (Chapter 9) to the formation of resins by the action of aluminum chloride on highly cracked gasolines containing aromatic, diolefin and olefin hydrocarbons.<sup>198</sup> Such resins are probably the result of simultaneous polymerization of monolefin and diolefin hydrocarbons and also condensation of diolefins with aromatics. The product is amber-colored, melts at 230-240°F. (ring and ball method), is soluble in practically all hydrocarbon solvents but insoluble in methyl or ethyl alcohol and acetone. It is neutral, possesses an iodine number of 130-160 and a saponification value of 5-15 (see Fig. 52). The resin dissolves readily in

<sup>196</sup> C. C. Furnas, *Ind. Eng. Chem., Anal. Ed.*, 1929, 1, 185.

<sup>197</sup> C. R. Wagner and J. Hyman, *loc. cit.* These investigators also noted the marked accelerating action of strong acids, such as hydrochloric acid, on gum-formation.

<sup>198</sup> C. A. Thomas and W. H. Carmody, *Ind. Eng. Chem.*, 1932, 24, 1125. C. A. Thomas and C. A. Hochwalt, U. S. P. 1,836,629, Dec. 15, 1931, to Dayton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1932, 26, 1144. French P. 679,402, 1929, to Thomas & Hochwalt Laboratories, Inc.; *Chem. Abs.*, 1930, 24, 39'5. French P. 723,070, 1931, to Dayton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1932, 26, 4191. British P. 340,001, 1929, to Thomas & Hochwalt Laboratories, Inc.; *Chem. Abs.*, 1931, 25, 2867. C. A. Thomas and W. H. Carmody, U. S. P. 1,932,708, to Dayton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1935, 29, 523. F. W. Sullivan, Jr., V. Voorhees, A. W. Neeley and R. V. Shankland, *Ind. Eng. Chem.*, 1931, 23, 604. M. Jeanny, *Rev. gen. nat. plastiques*, 1934, 10, 306; *Chem. Abs.*, 1934, 28, 7041. A. D. Camp, *Chem. Met. Eng.*, 1934, 41, 123.

linseed or tung oil and yields quick-drying varnishes. The chief advantages are stated to be fastness to light and speed of drying when incorporated with drying oils. The varnish films display a tendency to bleach.

In refining cracked gasolines with adsorbent earths, such as fuller's earth, various clays, bauxite or activated carbon, polymerization of reactive unsaturated hydrocarbons takes place on the surface of the contact material.<sup>199</sup> In one method, gasoline is vaporized and passed through the adsorbent at a temperature of about 200°C. This yields a refined gasoline and leaves gummy and resinous polymers in the adsorbent so that frequent revivification becomes necessary. Another procedure consists in conducting liquid gasoline through a bed of refining material maintained at 100°C. and redistilling the filtrate. Polymers and gums are washed out of the contact mass and recovered by evaporation of the solvent. In this manner the effectiveness of the polymerizing agent is prolonged. Vapor-phase refining of cracked gasolines is more generally utilized especially at temperatures above 200°C. and at superatmospheric pressures.<sup>200</sup> Cracked gasoline is treated also with clay at 600-650°F. and 1000 pounds pressure. The mixture is then passed to a vaporizing drum, and gasoline distilled from clay and polymers by reduction in

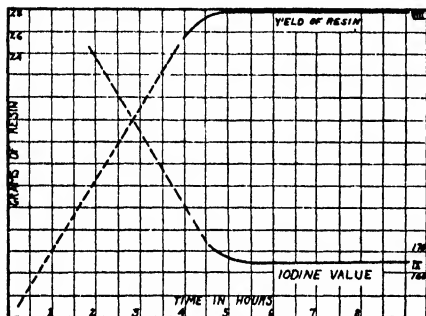


FIG. 52.

Effect of Time on Yield (g. per 100 cc.) and Iodine Number of Resin from Cracked Gasoline by Treatment with Aluminum Chloride. (C. A. Thomas and W. H. Carmody.)

Courtesy Industrial and Engineering Chemistry

pressure.<sup>201</sup> In addition to the previously mentioned materials, pumice stone, Floridin and silica gel promote polymerization.<sup>202</sup> Brooks<sup>203</sup> noted pronounced ability of certain sedimentary rocks of Oklahoma to effect polymerization of hydrocarbons. Several were nearly equal to the best grades of fuller's earth.

Gray and Mandelbaum<sup>204</sup> passed the vapors of gasoline containing diolefins and other unstable hydrocarbons through an adsorbent catalyst, Floridin earth of 60-90 mesh. They found that polymerization occurred accompanied by formation of high-boiling liquids. These polymers were yellow to ruby-red or green viscous oils or resinous substances and amounted to 0.3-1.0 per cent of the distillate treated. In one instance, after separation of gasoline, the residual polymers were fractionated under 0.2 mm. pressure and yielded a fraction boiling at 300-400°F. and a semi-solid tacky residue. The physical properties of the former, which was unsaturated (iodine number of 200), corresponded with those of a lubricant. Incorporation of the thick residues with linseed or tung oil and addition of a

<sup>199</sup> See, e.g., A. E. Dunstan, F. B. Thole and F. G. P. Remfray, *J.S.C.I.*, 1924, 43, 179T. F. G. P. Remfray, British Patents 208,868 and 212,500; *Chem. Abs.*, 1924, 18, 1195, 2245. H. Gault and R. Sigwalt, *Ann. office nat. comb. liquides*, 1927, 2, 309, 543; *Chem. Abs.*, 1928, 22, 379.

<sup>200</sup> D. F. Gerstenberger, *Nat. Pat. News*, 1931, 23 (6), 59; *Chem. Abs.*, 1931, 25, 2842.

<sup>201</sup> W. W. Holland, *Refiner*, 1932, 11 (1), 26; *J. Inst. Pet. Tech.*, 1932, 18, 86A.

<sup>202</sup> H. I. Waterman and J. H. J. Perquin, *J. Inst. Pet. Tech.*, 1926, 12, 506. H. I. Waterman and J. C. Jamn, *ibid.*, 1912, 12, 510. R. C. Geddes, *Gas World*, 1931, 94 (Coating Sect.), 9; *Chem. Abs.*, 1931, 25, 2270. M. R. Mandelbaum and R. S. Nilsson, *Ind. Eng. Chem.*, 1926, 18, 504.

<sup>203</sup> B. T. Brooks, *Petr. Eng.*, 1930, 1 (9), 191.

<sup>204</sup> T. T. Gray and M. R. Mandelbaum, *Ind. Eng. Chem.*, 1924, 16, 913.

japan drier yields a varnish.<sup>205</sup> On the other hand, treatment of the light ends (those boiling below 113°C.) of vapor-phase-cracked gasoline with activated clay gives a pale yellow product. Distillation of the latter leaves a residual, transparent, rapidly drying oil.<sup>206</sup>

Dunham<sup>207</sup> obtained a resinous product by conducting hydrocarbon vapors, having 5-10 per cent of diolefins, through bauxite, fuller's earth, animal or vegetable charcoal or porous clay, heated to about 200°C. The resin, representing a nearly quantitative conversion of the diolefins, was molten at this temperature, flowed through the contact mass, and was withdrawn. It solidified to a brittle substance, in appearance somewhat resembling the darker varieties of colophony. It was soluble in alcohol, benzol and acetone, slightly so in ether and about 50 per cent dissolved in gasoline. The resin is suggested for varnish manufacture, for insulating compositions, and may be vulcanized with sulphur.

Refining of gasoline, naphtha, burning and lubricating oils at high temperatures with finely divided substances is described by Leslie and Barbre.<sup>208</sup> Oil is run into a digester provided with reflux, and polymerizing agents then added. The latter may be fuller's earth, kieselguhr, clay, charcoal or powdered coke mixed with an alkaline substance, e.g., calcium carbonate. Alternate refluxing and distillation is employed, some distillate being eliminated after each refluxing treatment. As the more volatile fractions are gradually distilled, the temperature of refluxing rises. Combined treatment in this fashion ultimately gives a product which, after removal of heavy oils by steam distillation, yields a residue exhibiting resinous properties.<sup>209</sup> Smith and Ziser<sup>210</sup> suggest allowing cracked distillates to age for about 2 weeks, extracting any petroleum acids formed with alkalies, and then removing resins by adsorbent earths.

Resinous polymerized hydrocarbons which remain on the contact materials can be extracted by solvents such as a mixture of alcohol and ether or liquid sulphur dioxide.<sup>211</sup> These extracted substances may be added to lubricating oils to bring the latter to a standard color.<sup>212</sup>

Morrell and Egloff<sup>213</sup> subject the resinous substances, recovered from spent adsorbents, either to the action of oxidizing agents (air, oxygen or ozone) at slightly elevated temperatures, or to the polymerizing effect of salts such as ferric, zinc or stannic chloride, or to a combined treatment of both. Hard resins can be obtained which may be employed for varnish, paint, insulating films or fillers. A modification of the above procedure consists in oxidizing in the presence of phenolic compounds.<sup>214</sup> For example, a mixture of equal parts of resinous polymers and phenols or tar acids is heated to 300°F. in a current of air, until the mixture at-

<sup>205</sup> M. B. Chittick, U. S. P. 1,891,079, Dec. 13, 1932, to Pure Oil Co.; *Chem. Abs.*, 1933, 27, 2051. See also G. Zilberman, A. A. Bolotin and S. Yakubovich, *Lakokrasochnyy Ind.*, 1933 (1), 37, *Chem. Abs.*, 1933, 27, 4695. G. Zilberman, S. V. Yakubovich, A. A. Bolotin and M. I. Micheva, *J. Chem. Ind. (Moscow)*, 1933 (4), 16; *Chem. Abs.*, 1933, 27, 5558.

<sup>206</sup> J. Hyman, U. S. P. 1,919,722, July 25, 1933, to Velsicol Corp.; *Brit. Chem. Abs.* B, 1934, 462.

<sup>207</sup> H. V. Dunham, U. S. P. 1,324,649, Dec. 9, 1919; *J.S.C.I.*, 1920, 39, 164A. *British P.* 138,046, 1919; *J.S.C.I.*, 1920, 39, 342A.

<sup>208</sup> E. H. Leslie and C. Barbre, U. S. P. 1,337,523, Apr. 20, 1920, to General Petroleum Corp.; *Chem. Abs.*, 1920, 14, 1895.

<sup>209</sup> Carleton Ellis and J. V. Meigs, "Gasoline and Other Motor Fuels," D. Van Nostrand Co., New York, 1921, 120.

<sup>210</sup> F. H. Smith and G. J. Ziser, U. S. P. 1,507,692, Sept. 9, 1927, to Standard Oil Co. of Calif.

<sup>211</sup> J. C. Morrell, U. S. P. 1,608,135, Nov. 23, 1926, to Universal Oil Products Co.; *Chem. Abs.*, 1927, 21, 318. See also T. T. Gray, *British P.* 249,871, Mar. 24, 1925; *Chem. Abs.*, 1927, 21, 1007.

<sup>212</sup> C. C. Miller, U. S. P. 1,869,608, Aug. 3, 1932, to Standard Oil Development Co.; *Brit. Chem. Abs.* B, 1933, 499. Cf. Geiman P. 582,173, 1933, to Standard Oil Development Co.; *Chem. Abs.*, 1933, 27, 5182. A method for incorporating resins with oils is described by M. B. Hopkins, U. S. P. 1,948,267, Feb. 20, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1934, 28, 2884.

<sup>213</sup> J. C. Morrell and G. Egloff, U. S. P. 1,627,054, Mar. 3, 1927, to Universal Oil Products Co.; *Chem. Abs.*, 1927, 21, 2186.

<sup>214</sup> J. C. Morrell and G. Egloff, U. S. P. 1,766,927, Jan. 24, 1930, to Universal Oil Products Co.; *Chem. Abs.*, 1930, 24, 4409.

tains the desired viscosity or hardness. Action of the oxidizing agent is promoted by ultraviolet or actinic light.<sup>215</sup> An alternate procedure is chlorination of the resin phenol mixture.<sup>216</sup>

Resinous polymerized hydrocarbons are obtained by treatment of cracked distillates, particularly those containing diolefins, with hot concentrated aqueous zinc chloride,<sup>217</sup> pumice saturated with an alcoholic solution of zinc chloride,<sup>218</sup> stannous chloride<sup>219</sup> and aluminum chloride.<sup>220</sup> For example, with the last-named agent a drying-oil substitute, a mixture of polymerized olefins and diolefins, may be obtained as a by-product in the refining of highly cracked distillates.<sup>221</sup> In the case of aluminum chloride very resinous and sticky polymers often are formed which are difficult to remove from the reactor and involve loss of the metallic chloride. Double compounds of aluminum chloride and olefins (e.g.,  $\text{AlCl}_3 \cdot \text{C}_2\text{H}_4$ ) may be employed also.<sup>222</sup>

Although refining with sulphuric acid is still extensively practiced, large losses of hydrocarbons accompanied by formation of tars and resins often are experienced with highly cracked distillates.<sup>223</sup> To minimize such losses the use of dilute acid of various concentrations has been proposed.<sup>224</sup> Polymerization of the lower-boiling fractions of vapor-phase-cracked gasoline with dilute acid to give drying-oil substitutes is described by Hyman.<sup>225</sup> Amber-colored resins are reported to be obtained by treating petroleum distillates (containing a large proportion of olefins) with 90-95 per cent acid at 95-105°F., removing the acid-sludge and steam-distilling it after neutralization.<sup>226</sup> Such resins may be hardened by treatment with cresylic acid or formaldehyde in the presence of ammonia.

Attempts have been made to utilize the tars and resinous by-products of refining as raw materials for the production of asphalts. The difficulty attending such utilization appears to be the complete removal of sulphuric and sulphonic acids or sulphuric esters. Wilhelm<sup>227</sup> makes a neutral composition by the action of sulphur or hydrogen sulphide on acid tars at 130°C. The sulphuric acid present is reduced to sulphur which in turn accelerates resinification of the mass. Such bitumen is said to be adaptable for use in street paving, in the preparation of

<sup>215</sup> J. C. Morrell, U. S. P. 1,888,044, Nov. 15, 1932, to Universal Oil Products Co.; *Chem. Abs.*, 1933, 27, 1530.

<sup>216</sup> J. C. Morrell and G. Egloff, U. S. P. 1,744,135, Jan. 21, 1930, to Universal Oil Products Co.; *Chem. Abs.*, 1930, 24, 1529.

<sup>217</sup> A. Lachman, *Oil and Gas J.*, 1931, 30 (26), 30; *Chem. Abs.*, 1932, 26, 1425. *Petroleum World*, 1931, 28 (11), 23; *Chem. Abs.*, 1932, 26, 2044. *Refiner*, 1931, 10 (11), 72; *Chem. Abs.*, 1932, 26, 3097. A. Ya. Kubulnek, *Neft. Khoz.*, 1932, 22, 104; *Chem. Abs.*, 1932, 26, 4455. F. E. Kimball, U. S. P. 1,917,048, July 11, 1933; *Brit. Chem. Abs. B*, 1934, 310.

<sup>218</sup> A. E. Dunstan, British P. 327,421, Oct. 4, 1928, to Anglo-Persian Oil Co.; *Brit. Chem. Abs. B*, 1930, 599.

<sup>219</sup> A. Mailhe, *Compt. rend.*, 1925, 181, 668; *Chem. Abs.*, 1926, 20, 497.

<sup>220</sup> A. E. Dunstan, British P. 119,751, 1917; *J.S.C.I.*, 1918, 37, 727A. A. E. Dunstan and R. Pitkethly, *J. Inst. Pet. Tech.*, 1934, 10, 728. S. Stransky and F. Hansgig, British P. 287,950, 1927; *Brit. Chem. Abs. B*, 1928, 633.

<sup>221</sup> One oil of this type, Puresinol, is described as having sp.gr. 0.956, Saybolt viscosity (at 100°F.) 200 sec., and iodine number 175 (*Ind. Eng. Chem.*, 1934, 26, 9). See also French P. 680,038, 1929, to Pure Oil Co.; *Chem. Abs.*, 1930, 24, 3799. French P. 759,089, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3228.

<sup>222</sup> H. Häuber, German P. 557,305, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 304. See also British P. 345,334, 1929, and 413,007, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 155; 1935, 29, 523.

<sup>223</sup> For resin-formation during acid treating of cracked distillates containing unsaturated hydrocarbons, see A. Ufer, British P. 251,117, 1925, to Ges. für Warmetechnik; *Chem. Abs.*, 1927, 21, 1348. A. S. Ramage, U. S. P. 1,483,835, Feb. 12, 1924; *Chem. Abs.*, 1924, 18, 1194. Wöbling, *Braunkohle*, 1922, 21, 453; *Chem. Abs.*, 1923, 17, 206. B. Melis, *Ann. chim. applicata*, 1928, 18, 108; *Chem. Abs.*, 1928, 22, 3060.

<sup>224</sup> See, for example, H. J. Halle, U. S. P. 1,681,638, Aug. 21, 1928, to Universal Oil Products Co.; *Chem. Abs.*, 1928, 22, 3984. V. Voorhees and E. J. Schaffer, U. S. P. 1,810,632, June 16, 1931; *Brit. Chem. Abs. B*, 1932, 412. Carleton Ellis, U. S. P. 1,328,061, Oct. 7, 1919, to Ellis-Foster Co.; *J.S.C.I.*, 1919, 38, 891A.

<sup>225</sup> J. Hyman, U. S. P. 1,919,723, July 25, 1933, to Velsicol Corp.; *Chem. Abs.*, 1933, 27, 4942.

<sup>226</sup> F. Look, *Oil News*, 1934 35, 138; *J. Inst. Pet. Tech.*, 1934 20, 548A; 1935, 21, 439.

<sup>227</sup> F. Wilhelm, British P. 254,674, 1925; *Brit. Chem. Abs. B*, 1927, 596.

roof boards, for the manufacture of varnish and briquette resins as well as for the generation of liquid asphalt.<sup>228</sup>

In the Hamburger process<sup>229</sup> acid sludge is heated at 80-100°C. until stratification into three layers occurs; a top layer of oil, an intermediate bituminous layer, and a bottom layer of sulphuric acid. The bituminous layer is separated and then freed of acid by heating to 150° while a stream of air or steam, preheated to 170-200°C., is passed through it. Benesch<sup>230</sup> suggests heating acid sludge only to 50°C. to effect stratification. The intermediate layer is removed, mixed with silica, sawdust or other inert material and extracted with organic solvents (ether, alcohols, esters or ketones) in a Soxhlet apparatus. Two liquid layers are obtained, of which the lower is mainly sulphuric acid and the upper consists of a solution of resin in the solvent. To remove the last traces of acid, the process can be repeated. Evaporation of the solvent yields the resin.

Pickering<sup>231</sup> makes a neutral resin from acid sludge by extraction with hot acetone, or other water-soluble organic solvent, followed by dilution of the acetone solution with water. Acetone is distilled off and aqueous sulphuric acid is withdrawn. The insoluble resinous material is washed with a dilute aqueous solution of sodium chloride or carbonate, and finally heated to 125°C. to eliminate all traces of solvents.

In another procedure the tar acids from refining cracked distillates are diluted first with water and then with aqueous alkali.<sup>232</sup> The latter is waste liquid from washing acid-refined benzines. Separation into two layers occurs. The upper oily layer is removed, neutralized and distilled with steam. The fraction boiling between 200° and 280°C. is heated with manganese or cobalt driers to give a varnish-like product. It may be polymerized also to hydrocarbons of high molecular weights. Treatment of the still residue with steam and air furnishes an asphalt-like substance (soluble in benzene) which may be used in lacquers.

Polymerization of mineral oils with sulphuric acid, in the presence of a small proportion of caoutchouc which acts as a priming agent, yields an elastic mass capable of being vulcanized.<sup>233</sup>

#### MISCELLANEOUS PROCESSES

Auer<sup>234</sup> proposed heating oils containing unsaturated hydrocarbons with acids, their salts, or organo-metallic compounds. The resulting mass afterwards may be subjected to the action of ultraviolet light. For example, mineral oil is heated to 300-350°C., under reduced pressure, with cobalt linolate and potassium thiocyanate. The resinous bodies so formed may be employed in the manufacture of varnish, rubber, soap or candles.

According to Arnot,<sup>235</sup> fluid compositions which harden on use are made by mixing a large proportion of tar and asphaltic bitumen with a cracked distillate boiling above 190°C. The unsaturated hydrocarbons in the latter resinify or polymerize with those present in tar or bitumen under the influence of atmospheric oxygen.

<sup>228</sup> C. Sautermeister and F. Wilhelm, U. S. P. 1,677,731, July 17, 1928; *Chem. Abs.*, 1928, 22, 3290. French P. 606,817, 1925; *Brit. Chem. Abs. B*, 1927, 182.

<sup>229</sup> S. Hamburger, British P. 359,461, 1930; *Brit. Chem. Abs. B*, 1932, 9.

<sup>230</sup> E. Benesch, German P. 388,467, 1922; *J.S.C.I.*, 1924, 43, 366B.

<sup>231</sup> J. Pickering, British P. 279,613, 1926; *Brit. Chem. Abs. B*, 1928, 6.

<sup>232</sup> W. dePiotrowsky and J. Winkler, British P. 309,718, 1928, to Galicyjskie Towarzystwo Naftowe Galicja Soc. Anon.; *Chem. Abs.*, 1930, 24, 719.

<sup>233</sup> E. Kleiber and P. Gilardi, Swiss P. 146,279, 1929; *Chem. Abs.*, 1932, 26, 337.

<sup>234</sup> L. Auer, French P. 652,796, 1926; *Chem. Abs.*, 1929, 23, 3504. *Rev. gen. mat. plastique*, 1929, 5, 315; *Chem. Abs.*, 1929, 23, 455.

<sup>235</sup> R. Arnot, U. S. P. 1,847,805, March 1, 1932; *Chem. Abs.*, 1932, 26, 2569.

DeGiron<sup>230</sup> developed a process for the manufacture of rubber-like materials which consists in mixing petroleum fractions boiling at 280-370°C. (atmospheric pressure) with the aqueous portion of the fermentation products of hay or molasses. The mixture is aerated in direct sunlight for 70-80 hours. One to two per cent of a base, e.g., magnesium oxide, and 0.5-1.0 per cent of sulphur monochloride or 1-6 per cent of sulphur, are added and the mass heated to 115-120°C. If exposure of the mixture of oil and fermented liquor is continued for 90-100 hours longer, 75-85 per cent of the oil is converted into fatty acids which may be employed in the manufacture of soap.

Molding compositions for electrical insulation or as compounding ingredients in rubber goods are prepared by Winkelmann<sup>237</sup> by blowing a heated mixture of petroleum oil flux, asphalt and pine tar with air.

Tarry residues (as well as gaseous and liquid products) are obtained by the thermal decomposition at 496°C. of thioethers, mercaptans or disulphides.<sup>238</sup>

#### EFFECT OF LIGHT

The effect of light on petroleum products, especially cracked distillates or those containing olefins, appears to be that of polymerization or an acceleration of oxidation reactions, or probably a combination of both. The action of sunlight in promoting the gumming of cracked gasolines has been mentioned previously. These effects are indicated also by the work of Ostrejko<sup>240</sup> and of Carpenter<sup>240</sup> on the color changes observed during the exposure of petroleum oils to sunlight.

Mardles and Moss<sup>241</sup> increased the gum content of cracked gasoline by exposing samples in quartz tubes (half-filled) to the action of ultraviolet light. Freund<sup>242</sup> noted that resin formation increased with time of exposure. He believed that the source of such materials were complex unsaturated hydrocarbons and not paraffins, naphthenes, aromatics or simple olefins. Absorption of oxygen was considered to be of secondary importance. However, Vellinger and Radulesco<sup>243</sup> state the rate of absorption of oxygen by cracked distillates during irradiation (with mercury light) in pyrex glass vessels paralleled the amount of gum formed, some samples absorbing more than thirty volumes of the gas. Oils exhibiting the longer induction period yielded the smaller quantity of gum.

Increase in viscosity (by polymerization) is effected by treatment of oils, in either the liquid or vapor phase, with light from a mercury vapor lamp.<sup>244</sup> Ellis<sup>245</sup> deblooms lubricating oils with ultraviolet light in the presence of an inert gas, e.g., nitrogen, to prevent oxidation. In this manner the resin-forming constituents are polymerized. In the latter operation substitution of air for nitrogen results not only in the oil being debloomed but also a substantial proportion is converted to acids and esters.<sup>246</sup> Tauss<sup>247</sup> suggests, as a refining procedure, accelerating polymerization of resin-forming constituents by treating heated oil with a small proportion of oxygen. Reaction is catalyzed further by irradiation, the glow discharge or addition of alkalies or acids.

<sup>230</sup> J. T. deGiron, U. S. P. 1,835,998, Dec. 8, 1931; *Brit. Chem. Abs. B*, 1932, 911. French P 728,602, 1931; *Chem. Abs.*, 1932, 26, 6184. See also *J. S.C.I.*, 1932, 51, 191.

<sup>237</sup> H. A. Winkelmann, U. S. P. 1,709,242, Apr. 16, 1929, to Philadelphia Rubber Works Co. *Chem. Abs.*, 1929, 23, 2272.

<sup>238</sup> W. F. Faragher, J. C. Morrell and S. Comay, *Ind. Eng. Chem.*, 1928, 20, 527.

<sup>240</sup> R. A. Ostrejko, *Trudy. bak. otd. imp. russk. tech. obschtsch.*, 1895, 10 (2), 21; 1895, 10 (4) 19; 1896, 10 (6), 1; *J. S.C.I.*, 1896, 15, 26, 345, 645.

<sup>240</sup> J. A. Carpenter, *J. Inst. Pet. Tech.*, 1928, 12, 518.

<sup>241</sup> E. W. J. Mardles and H. Moss, *J. Inst. Pet. Tech.*, 1929, 15, 657.

<sup>242</sup> M. Freund, *Brennstoff-Chem.*, 1933, 14, 61; *Chem. Abs.*, 1933, 27, 3808.

<sup>243</sup> E. Vellinger and G. Radulesco, *Compt. rend.*, 1933, 196, 1495; *Brit. Chem. Abs. B*, 1933, 659.

<sup>244</sup> E. Goldstein, *British P.* 249,895, 1924; *Brit. Chem. Abs. B*, 1926, 526.

<sup>245</sup> Carleton Ellis, U. S. P. 1,989,359, Mar. 3, 1914, to Ellis-Poster Co.; *Chem. Abs.*, 1914, 8, 2501.

<sup>246</sup> T. T. Gray, U. S. P. 1,158,205, Oct. 26, 1915; *Chem. Abs.*, 1915, 9, 3358.

<sup>247</sup> J. Tauss, German P. 475,277, 1923; *Chem. Abs.*, 1929, 23, 3340.

Cracked gasoline may also be purified by submitting it to a mild treatment with aluminum chloride (1 per cent at 60-70°C.). The rest of the gum-forming substances are largely removed by exposing the material for 3 hours at room temperature to high-frequency alternating current discharges. Unsaturated compounds which exhibit a knock-decreasing effect are said to be retained in the gasoline.<sup>248</sup>

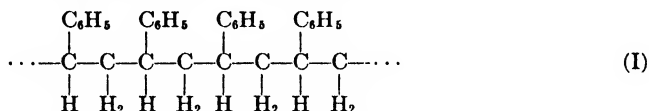
<sup>248</sup> F. Winkler and H. Haeubler, U. S. P. 1,990,213, Feb. 5, 1935, to I. G. Farbenind. A.-G.

## Chapter II

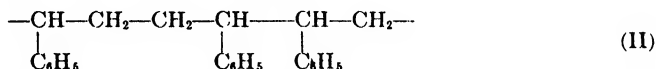
### Polystyrene and Related Resins

Styrene<sup>1</sup> ( $C_6H_5-CH=CH_2$ ), a colorless liquid boiling at  $143^\circ C$ ,<sup>2</sup> can be converted into a hard, colorless resin with attractive industrial and commercial possibilities. The resin, referred to here as polystyrene,<sup>3</sup> is the basis of commercial products which go under the trade names of Vietron,<sup>4</sup> Resoglaz,<sup>5</sup> and Trolitul.<sup>6</sup>

Polystyrene is one of the oldest synthetic resins, having been prepared by Simon<sup>7</sup> in 1839. Like most other resinification reactions the transformation of the liquid styrene to solid resin is one of polymerization:  $nC_6H_5 \rightarrow (C_6H_5)_n$ . Staudinger<sup>8</sup> represents the structure of polystyrene as a long chain of styrene groups formed by end-to-end combination at the olefinic double-bond, as follows:

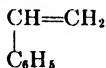


However, it is conceivable that instead of a symmetrical arrangement a more or less random union of styrene groups might result

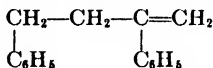


Pyrolytic products of polystyrene point to formula I as the correct structure of the polymer. That is, by heating polystyrene at atmospheric pressure at  $310-350^\circ C$ . for 6 hours or under high vacuum at  $290-320^\circ C$ . for 12 hours and fractionating the products, the following were identified:

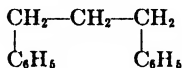
Styrene



Distyrene



1,3-Diphenylpropane



<sup>1</sup> Other names for this compound are styrol, styrolene, vinylbenzene, phenylethylene and cinnamene.  
<sup>2</sup> For other recently determined physical-chemical properties see S. Sabetay, *Bull. soc. chim.*, 1929, 45, 60; *Chem. Abs.*, 1929, 23, 2427. See also A. P. Aleksandrov, *J. Tech. Phys. (U. S. S. R.)*, 1933, 3, 823; *Chem. Abs.*, 1934, 28, 3061.

<sup>3</sup> The resin has been generally called "metastyrene," but to indicate its polymeric nature it seems advisable to dispense with the prefix "meta," which really denotes position of substitution in the benzene-ring, and to call it polystyrene as suggested by Staudinger.

<sup>4</sup> Naugatuck Chemical Company.

<sup>5</sup> Advance Solvents & Chemical Corp.

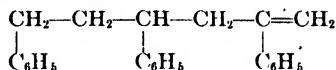
<sup>6</sup> I. G. Farbenindustrie A.-G.

<sup>7</sup> E. Simon, *Ann.*, 1839, 31, 267.

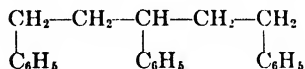
<sup>8</sup> H. Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932, 162.



Tristyrene



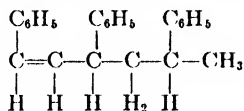
1,3,5-Triphenylpentane



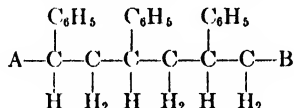
In no case were compounds isolated which would correspond to the structure II as a source.<sup>8a</sup>

Polystyrene is thus a long methylene-chain substituted alternately by phenyl groups. This conception of the molecular structure is confirmed by measurements of light-absorption<sup>9</sup> and Raman spectra<sup>10</sup> of solutions which indicate an alkylbenzene structure for the polymer. Also, theoretical considerations based on the determination of the streaming double refraction<sup>11</sup> of dilute solutions of polystyrene show, at least for the lower polymers, that the dissolved molecules are straight threads.<sup>12</sup> It has been estimated that in the more-highly polymerized forms there may be several thousand styrene units in the chain.<sup>13</sup>

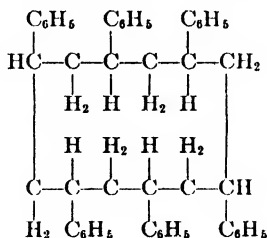
The end valences may be satisfied by: (1) migration of an H-atom from one end of the chain to the other, or from one molecule to another:



(2) combination with a catalyst A-B, or solvent molecules and impurities present:



or (3) cyclization, ring formation by union of the two ends of the chain. The structure would then become a flattened ring or double chain:



The question of the nature of the end groups of the polystyrene chain is still undecided. The end carbons are not trivalent and the molecule does not appear to be cyclic. Although there is the possibility of ring formation at the ends of the chains similar to the rings shown by Bergmann<sup>14</sup> to occur in the dimerization

<sup>8a</sup> H. Staudinger and A. Steinhilber, *Ann.*, 1935, 517, 35.

<sup>9</sup> J. H. deBoer, R. Houwink and J. F. H. Custers, *Rec. trav. chim.*, 1933, 52, 709; *Chem. Abs.*, 1933, 27, 5004.

<sup>10</sup> R. Signer and J. Weiler, *Helv. Chim. Acta*, 1932, 15, 649; *Chem. Abs.*, 1932, 26, 5497. Cf. J. H. Hubben, *Ind. Eng. Chem.*, 1934, 26, 646.

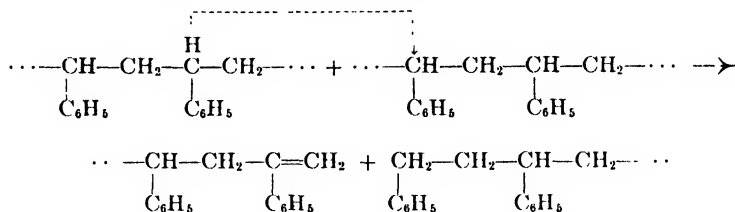
<sup>11</sup> See Chapter 3.

<sup>12</sup> R. Signer and H. Gross, *Z. physik. Chem.*, 1933, 165, 161; *Brit. Chem. Abs. A*, 1933, 902.

<sup>13</sup> R. Signer and H. Gross, *Helv. Chim. Acta*, 1934, 17, 355; *Chem. Abs.*, 1934, 28, 4287. See also *ibid.*, 1934, 17, 59, 726; *Chem. Abs.*, 1934, 28, 4709, 6047.

<sup>14</sup> E. Bergmann, *Ann.*, 1930, 480, 49; *Ber.*, 1931, 64, 1493.

of asym-diphenylethylene and  $\alpha$ -methylstyrene, Staudinger and Steinhof<sup>15</sup> consider it more likely that the molecule contains a double bond at one end, the mechanism of its formation involving the wandering of a hydrogen atom from the end of one chain to saturate the end of another as follows:



However, attempts to determine unsaturation by bromine absorption were unsuccessful, as well as reactions in which styrene was polymerized, or polystyrene was depolymerized, in the presence of various substances such as hydriodic acid, acetic acid, acetic anhydride, chloroform and piperidine which would be expected to add to double bonds. The final product in each case was a hydrocarbon and contained no detectable extraneous group.

#### POLYMERIZATION

Styrene may be polymerized in various ways. The change may be brought about simply by heating, catalysts may be added which accelerate the reaction, or it may occur in presence of other substances not catalysts. Styrene may be heated in an inert solvent, with or without a catalyst, or the solvent may be one that itself polymerizes or assists in the polymerization. Co-polymerization or heteropolymerization (see Chapter 4) may be utilized to produce special properties in the final polymerized product. Emulsions may be heated to form an artificial latex. In all cases, substances such as softeners, dyestuffs, fillers and pigments, may be added to modify the nature and appearance of the plastic.

Kronstein<sup>15a</sup> heated styrene in a sealed glass tube and observed that polymerization progressed in two stages. Thickening occurred gradually during the first stage and after a certain period gelatinization<sup>16</sup> suddenly set in. Polymerization is a continuous reaction in which the molecular weight and softening point of the polymer gradually increase. The apparent discontinuity noted by Kronstein is explained by the assumption that gelatinization occurs as soon as the softening point of the polymer is higher than the temperature at which the reaction tube is being heated.

#### CLASSIFICATION OF POLYMERS

Products of different properties are obtained by polymerization at a high temperature or at a low temperature. Also the properties are dependent upon the presence of a catalyst, the products of catalytic polymerization being comparable to those obtained at a higher temperature. Ostromislensky<sup>16a</sup> designated the products of low-temperature polymerization as alpha-metastyrol; high-temperature products, beta-metastyrol; and those obtained by use of catalysts, gamma-metastyrol.

<sup>15</sup> H. Staudinger and A. Steinhof, *Ann.*, 1935, 517, 35.

<sup>15a</sup> A. Kronstein, *Ber.*, 1903, 35, 4154.

<sup>16</sup> L. Auer considered this phenomenon analogous to the thickening of drying oils. See *Chem. Umschau*, 1926, 33, 216; *Brit. Chem. Abs.* B, 1926, 888.

<sup>16a</sup> I. Ostromislensky, U. S. P. 1,683,402, Sept. 4, 1928, to Naugatuck Chemical Co.; *Chem. Abs.*, 1928, 22, 3893.

Staudinger<sup>17</sup> adopted a different basis of classification. He found that all distinctions could be traced to differences in molecular weight; or, stated in another way, to differences in length of the chains formed by the polymerization reaction. He classified the polymers therefore as eucolloidal polystyrene (long chains of high molecular weight), and hemicolloidal polystyrene (short chains of relatively low molecular weight).<sup>18</sup>

The product of polymerization is not a single substance but a mixture of homologues of varying chain-length. Molecular weight determinations give only average molecular sizes. The mixture may be separated into fractions showing different molecular weights, whose solutions differ in viscosity,<sup>19</sup> and whose toughness and strength in massive form vary considerably. In fact all the properties of polystyrene are functions of the average molecular weight of the substance.<sup>20</sup>

### LOW-TEMPERATURE POLYMERIZATION

Polymerization occurs more slowly at low temperatures than at high, but the low-temperature product has a much higher molecular weight. Blyth and Hofmann<sup>21</sup> observed that styrene changed to polystyrene on heating at water-bath temperature for 3 days, whereas only a half hour was required at a temperature of 200°C. Ostromislensky<sup>22</sup> heated styrene in sealed tubes at a moderate temperature for a period which varied according to the temperature used. He suggested heating for 20 hours at 140°C., 18 hours at 155°, 16 hours at 165° or 10 hours at 175° to produce the resin.

Pure styrene at room temperature polymerizes extremely slowly and may be kept several years with only partial polymerization. Staudinger<sup>23</sup> separated the polymerized portion from a sample which had been standing for some time and found that the resin was much tougher than polystyrene prepared at higher temperatures, did not soften until heated above 200°C. and gave a highly viscous solution in benzene, the material swelling before it dissolved. The molecular weight was 350,000, indicating that about 3000 molecules of styrene had combined to form the average resin molecule. Solutions of polystyrene of such high molecular weight show pronounced colloidal properties. The solubility and swelling power of polystyrenes are apparently related to their molecular structure. Staudinger and Heuer<sup>24</sup> found that styrene polymerized with 1 per cent of p-divinylbenzene forms an insoluble resin. It is their belief that polymers of this type have 3-dimensional molecules, while those that swell in organic solvents have thread molecules. The p-divinylbenzene may be present as an impurity, formed when styrene is produced by the dehydrogenation of ethylbenzene containing small amounts of diethylbenzene.

### PROPERTIES OF POLYSTYRENE

Polystyrene resin obtained at a low or moderate temperature without a catalyst is water-white and transparent, remarkably tough, and shows a dull fracture when

<sup>17</sup> H. Staudinger, *Ber.*, 1929, 62, 2893; *Chem. Abs.*, 1930, 24, 1563.

<sup>18</sup> The isocolloid theory was first applied to polystyrene resins by Ostwald in 1922. See R. Houwink, *Kolloid-Z.*, 1934, 68, 371; *Chem. Abs.*, 1934, 28, 7580.

<sup>19</sup> H. Staudinger, M. Brunner, K. Fiey, P. Garbsch, R. Signer, and S. Wehili, *Ber.*, 1929, 62, 241; *Chem. Abs.*, 1929, 23, 2949. See also V. Z. Danes, *Kolloid-Z.*, 1934, 68, 110; *Chem. Abs.*, 1934, 28, 6359.

<sup>20</sup> H. Staudinger, W. Heuer and E. Husemann, *Z. physikal. Chem.*, 1934, 171, 129; *Brit. Chem. Abs. A*, 1935, 163. R. Signer, *Kolloid-Z.*, 1935, 70, 24; *Brit. Chem. Abs. A*, 1935, 162. A. Smakula, *Z. angew. Chem.*, 1934, 47, 777; *Chem. Abs.*, 1935, 29, 1073.

<sup>21</sup> Blyth and Hofmann, *Ann.*, 1945, 53, 311.

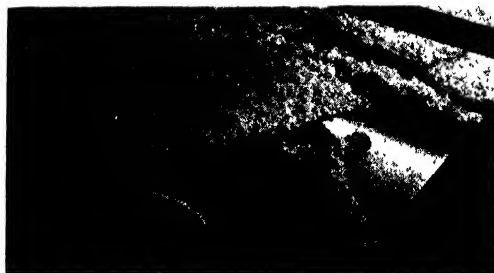
<sup>22</sup> I. Ostromislensky, U. S. P. 1,683,403, Sept. 4, 1928; *Chem. Abs.*, 1928, 22, 3893. British P. 236,891, 1925; *Chem. Abs.*, 1926, 20, 1243.

<sup>23</sup> H. Staudinger, *Z. physik. Chem.*, 1931, (A) 153, 410; *Chem. Abs.*, 1931, 25, 4847.

<sup>24</sup> H. Staudinger and W. Heuer, *Ber.*, 1934, 67, 1159, 1164; *Chem. Abs.*, 1934, 28, 6120. *Z. physik. Chem.*, 1935, (A) 171, 129; *Chem. Abs.*, 1935, 29, 2051. Cf. R. Signer and H. Gross, *Helv. Chim. Acta*, 1934, 17, 335; *Chem. Abs.*, 1934, 28, 4287.

broken (see Fig. 53). It can be cut into thin films and shavings but can be pulverized only with great difficulty. Average properties of the resin are: specific gravity, about 1.06; refractive index, from 1.50 to 1.75; hardness (Mohs), between 2 and 3; piercing potential, over 850 volts per mm.; and transverse tensile strength, about 6000<sup>28</sup> pounds per square inch. The resin is soluble in benzenoid hydrocarbons,<sup>29</sup> chlorinated hydrocarbons, cyclohexanone, ethyl and butyl acetate; insoluble in alcoholic solvents, glycol ethers, acetone, petroleum hydrocarbons and most acids and alkalis. The viscosity of the solutions varies with the molecular weight.

When heated, polystyrene first becomes elastic like rubber and at ordinary temperatures it may be compared with rubber that has been cooled to a very low temperature. It gives x-ray diffraction patterns, similar to those obtained with unstretched crude rubber,<sup>27</sup> characteristic of amorphous substances. Even when stretched to 400 or 500 per cent elongation the pattern is unchanged,<sup>28</sup> in contrast to rubber which when stretched shows regular crystalline interferences. In polystyrene a marked polarization may be observed.<sup>29</sup> A contrast may also



Courtesy Bakelite Corp.

FIG. 53.—Pieces of Polystyrene Resin.

be noted in the character of viscous solutions of polystyrene and rubber (or cellulose nitrate). The fundamental difference is considered to be in the shape of the particles.<sup>30</sup>

When heated to temperatures above 300°C. polystyrene is depolymerized to the monomer.<sup>31</sup> This reaction is not quantitative but is a convenient way of identifying the resin, for the styrene thus obtained may be converted into the characteristic dibromide, and it is a useful means of isolating styrene from a solution or complex mixture.<sup>32</sup> The material is heated until the polymer has formed, and this is recovered either by adding a non-solvent to precipitate it, or by distilling off all volatile liquids by means of steam. Destructive distillation of the resinous material then gives styrene. A small amount of the dimer (distyrene)<sup>33</sup> is formed simultaneously, which is removed by fractionating the distillate.

<sup>28</sup> Polystyrene sold under the name of "Victron" is stated to have a transverse tensile strength of 10,000-12,000 pounds per sq. in.

<sup>29</sup> In the determination of water in hydrocarbons, H. Broche and W. Scheer (*Brennstoff-Chem.*, 1933, 14, 408; *Brit. Chem. Abs. B*, 1934, 51) have used calcium chloride enclosed in capsules of polystyrene. When immersed in the hydrocarbon, the capsule dissolves.

<sup>27</sup> E. A. Hauser and P. Rosbaud, *Kautschuk*, 1927, 17; *Chem. Abs.*, 1927, 21, 1898.

<sup>28</sup> M. Hünemörder, *Kautschuk*, 1927, 106; *Chem. Abs.*, 1927, 21, 1898. See also G. S. Whitby, *India Rubber J.*, 1927, 73, 638; *Chem. Abs.*, 1927, 21, 2200.

<sup>29</sup> A. P. Aleksandrov, *J. Tech. Phys.*, 1933, 3, 823; *Chem. Abs.*, 1934, 28, 3061.

<sup>30</sup> I. Sakurada, *J. Soc. Chem. Ind. Japan*, 1934, 37, 473B; *Brit. Chem. Abs. A*, 1935, 163.

<sup>31</sup> Blyth and Hofmann, *Ann.*, 1845, 53, 315.

<sup>32</sup> I. Ostromislenskij, U. S. P. 1,703,950, March 5, 1929, to Naugatuck Chemical Co.; *Chem. Abs.*, 1929, 23, 1911. Canadian P. 265,325, 1928; *Chem. Abs.*, 1927, 21, 918.

<sup>33</sup> E. Erlenmeyer, *Ann.*, 1865, 135, 122. R. Fittig and H. Erdmann, *Ann.*, 1883, 216, 187. W. Königs

Polystyrene is resistant to most chemicals, even hydrofluoric acid and bromine having no effect on the solid resin. However, in solution it may be hydrogenated,<sup>34</sup> nitrated,<sup>35</sup> sulphonated<sup>36</sup> and chlorinated,<sup>37</sup> these reactions being confined to attack upon the phenyl groups.<sup>38</sup>

Laage<sup>39</sup> carried out the polymerization in the presence of a plasticizer to improve the flexibility of the product. He added 10 per cent ethylacetanilide and heated the mixture at 100°C. for 24 hours. Ostromislensky<sup>40</sup> dissolved a small amount of rubber in styrene and heated the solution at 140°C. The product had a nacreous luster similar to mother-of-pearl and was more flexible than the polystyrene made without admixture of rubber.

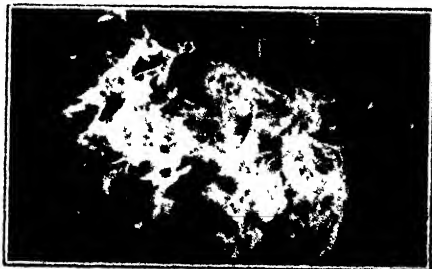


FIG. 54.

Polystyrene Eucolloid Prepared by H. Staudinger. Molecular Weight 440,000

Colored masses are obtained by dissolving fluorindenes or other dyestuffs in styrene and heating the solution. Addition of 0.5 per cent anthracene gives a violet fluorescence to the resin without affecting its transparency.<sup>41</sup> Amber-like bodies are formed by adding an azo-dye which decomposes during the heating to give a brown color.<sup>42</sup> Other kinds of coloring agents include colloidal metals, such as silver or gold, formed by thermal decomposition of metallic salts during the polymerization of styrene. The addition of 0.013 per cent of silver nitrate causes the resin to have a dark red color by transmitted light, and an opaque, gray shade by reflected light.<sup>43</sup> Spongy masses of low density suitable for heat-insulation are prepared by dissolution of gases (air, methyl chloride, carbon dioxide or dimethyl ether) under pressure in the molten resin and then releasing the pressure.<sup>44</sup>

Polystyrene is slightly permeable to moisture.<sup>45</sup> Tests have shown that the diffusion of water through polystyrene is twice that through hard rubber, gutta-percha or asphalt and about half that through soft vulcanized rubber. However, the amount of water actually absorbed is a small fraction of the quantity diffused.

and C. Mai, *Ber.*, 1892, 25, 2658. R. Stoermer and H. Kootz, *Ber.*, 1928, 61, 2330; *Chem. Abs.*, 1929, 23, 1397. E. Bergmann and H. Taubadel, *ibid.*, 1932, 65, 463; *Chem. Abs.*, 1932, 26, 2976.

<sup>34</sup> H. Staudinger, E. Geiger and E. Huber, *Ber.*, 1929, 62, 263; *Chem. Abs.*, 1929, 23, 2950. H. Staudinger and V. Wiedersheim, *ibid.*, 1929, 62, 2406; *Chem. Abs.*, 1930, 24, 3003. H. Staudinger, *German P.* 504,215, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5518.

<sup>35</sup> Blyth and Hofmann, *Ann.*, 1845, 53, 316.  
<sup>36</sup> C. Wulff, *German P.* 530,366, 1933; to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4816. *British P.* 367,416, 1930; *Brit. Chem. Abs. B.*, 1932, 591. A carbon tetrachloride solution is treated with chlorosulphonic acid to give wetting, emulsifying and sizing agents.

<sup>37</sup> H. B. Dykstra, U. S. P. 1,890,772, Dec. 13, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1643. *British P.* 364,873, 1931, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B.*, 1932, 494. See also C. Wulff, *German P.* 573,065, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2961.

<sup>38</sup> When dissolved in carbon tetrachloride and treated with ozone for a prolonged time, polystyrene gives an ozonide which may be hydrolyzed and the product oxidized to a substance of high molecular weight similar to polyacrylic acid. H. Staudinger and S. Wehrli, *Helv. Chim. Acta*, 1929, 12, 1124.

<sup>39</sup> E. Laage, *German P.* 487,707, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1947.

<sup>40</sup> I. Ostromislensky, U. S. P. 1,613,673, Jan. 11, 1927, to Naugatuck Chemical Co.; *Chem. Abs.*, 1927, 21, 806.

<sup>41</sup> I. Ostromislensky, U. S. P. 1,627,195, May 3, 1927; *Chem. Abs.*, 1927, 21, 2136.

<sup>42</sup> I. Ostromislensky, U. S. P. 1,613,674, Jan. 11, 1927; *Chem. Abs.*, 1927, 21, 806.

<sup>43</sup> I. Ostromislensky, U. S. P. 1,705,264, March 12, 1929, to Naugatuck Chemical Co.; *Chem. Abs.*, 1929, 23, 1911.

<sup>44</sup> C. G. Munters, *British P.* 406,267, 1932; *Brit. Chem. Abs. B.*, 1934, 384.

<sup>45</sup> D. B. Hermann, *Rubber Age* (N. Y.), 1934, 36, 73; *Chem. Abs.*, 1935, 29, 1174.

A tough polymer is obtained by heating styrene at an upper temperature limit of approximately 175°C. The product formed at higher temperatures does not have the pronounced colloidal characteristics of the eucolloidal polystyrene thus far described (See Fig. 54). Its molecular weight is progressively lower as the polymerization temperature is raised, since heavy organic molecules are less stable at a high temperature than lighter ones.

#### HIGH-TEMPERATURE POLYMERIZATION

The polymer resulting from reaction at high temperatures (above about 175°C.), or at lower temperatures for very long periods, is brittle in contrast to the tough product formed under less drastic conditions. Ostromislensky<sup>46</sup> heated styrene for 40 hours at 140°C. to yield a resin which he called beta-metastyrol. Also, by heating styrene for 18 hours at 170°C., 12 hours at 180°C., and 2 hours at 185°C., he obtained the same type of product. It was transparent but dark in color and gave a shiny and lustrous fracture like other brittle materials. It was

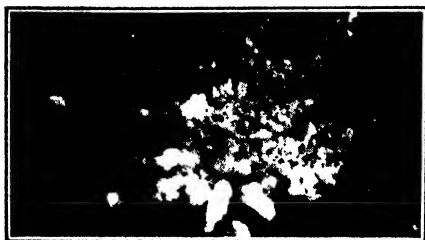


FIG. 55  
Polystyrene Hemicolloid Prepared by H. Staudinger. Molecular Weight 3,000.

too brittle to be cut or planed and could be pulverized easily. Its shock-resistance was low and its transverse tensile strength only about 1000 pounds per square inch. The same properties result when the tough eucolloid is heated to a high temperature.

Polystyrene formed at high temperatures is a hemicolloid (see Fig. 55). It dissolves very readily in all solvents in which the eucolloid is soluble, yielding solutions of low viscosity. Solubility in ether distinguishes it from the low-temperature polymer, which is insoluble or only partially soluble in this solvent. (See Table 25.)

The upper temperature limit<sup>47</sup> at which polystyrene may be obtained is about 300°C. Above this point the resin is depolymerized.

#### CATALYTIC POLYMERIZATION

Polymerization of styrene in the presence of catalysts generally produces resins similar to those obtained at high temperatures. The color, however, is usually better due to the lower temperatures used. The main advantage of catalytic polymerization is the greater speed at which the resin is formed.

A great many different agents have been suggested to accelerate the resinification. Most of them fall into the classes of oxidizing agents (oxygen, peroxides, peracids, ozone and ozonides), acids, metallic halides and alkalies. Also light has a polymerizing effect.

**Oxygen Catalysts.** Oxygen was one of the earliest catalysts employed. In

<sup>46</sup> I. Ostromislensky, U. S. P. 1,683,403, Sept. 4, 1928; *Chem. Abs.*, 1928, 22, 3893. British P. 236,891, 1925; *J.S.C.I.*, 1925, 44, 771B.

<sup>47</sup> When styrene is heated at 300-340°C. under low pressure, some naphthalene is formed as well as distyrene and higher polymers, according to H. Fischer and A. Treibs, *Ann.*, 1925, 446, 241; *Chem. Abs.*, 1926, 20, 1242.

fact, when Simon<sup>48</sup> noticed the transformation from a liquid to a solid he attributed it to oxidation and called the product "oxide of styrol." The reaction was regarded as analogous to the oxidation of linseed oil. Blyth and Hofmann<sup>49</sup> showed that oxygen was not essential for they obtained the resin by heating styrene in a sealed tube. However, oxygen is usually present when the resin is formed, especially when the reaction is carried out on a large scale, as by heating the liquid under a reflux condenser or in an autoclave, since there is always some air above the liquid.

TABLE 25.—*Physical Properties of Various Polystyrenes.\**

Material	Mol. Wt.	Degree of Polymerization	Appearance of Precipitate	Melting Point in °C.	Solubility in Ether	$\eta_{sp}/c$ 20°C.
Dimer. . . . .	208	2	Fluid	Fluid	Readily soluble	0 17
Trimer. . . . .	312	3	Fluid	Fluid	Readily soluble	0 24
Hemicolloid polymerized with SnCl <sub>4</sub> . . . . .	3,000	30	Brittle white powder	105-110	Soluble	0 78
Polymerized at 150°C. under N <sub>2</sub> . . . . .	23,000	230	White powder	120-130	Partly soluble	4 2
Polymerized at 100°C. under N <sub>2</sub> . . . . .	120,000	1200	White fibers	160-180	Insoluble	22.
Polymerized at room temperature in air . . . . .	200,000	2000	White fibers	>180*	Insoluble	39
Highest fraction polymerized at room temperature under N <sub>2</sub> . . . . .	600,000	6000	White fibers	>180*	Insoluble	110

\* H. Staudinger, "Die hochmolekularen organischen Verbindungen," Verlag von Julius Springer, Berlin 1932, 186.

\* The rate of fusion was very slow, and a definite temperature could not be fixed

There is a difference between polystyrene formed in the absence of air or oxygen and that formed in its presence. Styrene polymerized in absence of air produces very clear, vitreous resins which form much more viscous solutions than those of resins formed in contact with air.<sup>50</sup> When styrene is heated in the presence of oxygen the two reactions, oxidation and polymerization, occur simultaneously. Addition of cobalt compounds,<sup>51</sup> or of iodine and iodine compounds,<sup>52</sup> accelerates oxidation. Perbenzoic acid<sup>53</sup> speeds up both reactions. Anthracene on the other hand accelerates oxidation but inhibits polymerization.

The polymerization products of styrene formed in the presence of oxygen always contain small amounts of polymeric peroxides and produce traces of benzaldehyde when the resins are depolymerized.<sup>54</sup> Stobbe<sup>55</sup> found that styrene which had been exposed to light in the presence of oxygen gave benzaldehyde and formaldehyde as well as the polymer. Polymerization occurs more rapidly in oxygen than

<sup>48</sup> E. Simon, *Ann.*, 1839, 31, 267.

<sup>49</sup> Blyth and Hofmann, *Ann.*, 1845, 53, 291.

<sup>50</sup> H. Staudinger and H. Machemer, *Ber.*, 1929, 62, 2921; *Chem. Abs.*, 1930, 24, 1564.

<sup>51</sup> C. Dufraisse and D. Nakae, *Compt. rend.*, 1932, 194, 880; *Chem. Abs.*, 1932, 26, 2917.

<sup>52</sup> C. Moureau and C. Dufraisse, *ibid.*, 1924, 178, 824; *Chem. Abs.*, 1924, 18, 2635.

<sup>53</sup> N. A. Milas, *Proc. Nat. Acad. Sci.*, 1923, 14, 844; *Brit. Chem. Abs. A.*, 1923, 149. When styrene is oxidized by perbenzoic acid at a low temperature a good yield of styrene oxide is obtained according to H. Hibbert and C. P. Burt, *J.A.C.S.*, 1925, 47, 2243. See also "Styrene Oxide," in "Organic Syntheses," John Wiley & Sons, New York, 1928, VIII, 102.

<sup>54</sup> H. Staudinger and L. Lautenschläger, *Ann.*, 1931, 488, 1, *Brit. Chem. Abs. A.*, 1931, 1031.

<sup>55</sup> H. Stobbe, *J. prakt. Chem.*, 1914, 90, 551; *Chem. Abs.*, 1915, 9, 1174.

in an atmosphere of carbon dioxide. The addition of peroxides increases the rate of reaction but the effect is not as great as that of oxygen. It is concluded that an initial autoxidation product of styrene, a moloxide, is the actual catalyst when using oxygen.<sup>56</sup> Stobbe and Posnjak<sup>57</sup> observed that styrene that had stood for two weeks was more easily polymerized than freshly distilled material, probably because of autoxidation.

Ostromislensky,<sup>58</sup> by adding 1 per cent of benzoyl peroxide to styrene and heating the solution to 175°C. for an hour, obtained a brittle resin which he called  $\gamma$ -metastyrol to distinguish it from the polymers formed without a catalyst. Lawson<sup>59</sup> used benzoyl peroxide<sup>60</sup> with a solvent. Hydrogen peroxide<sup>61</sup> also has been recommended for use in emulsions. Other peroxides suggested include those of asym-diphenylethylene, cyclohexene, phellandrene<sup>62</sup> and triphenylmethyl.<sup>63</sup> Natelson<sup>64</sup> used benzoyl hydrogen peroxide, prepared in a nascent condition from benzaldehyde and an equivalent amount of oxygen. A 45 per cent solution of styrene in ethylbenzene was completely polymerized in 12 hours at 175°C. with 2 per cent of this catalyst. Barrett<sup>65</sup> obtained a product of low viscosity by heating styrene (or a vinyl ester) with benzoyl peroxide and rosin or a rosin ester at 110°C. and 500 lbs. pressure in a solvent naphtha solution.

Houtz and Adkins<sup>66</sup> studied polymerization in presence of the ozonides of a mixture of the two octylenes known as diisobutylene. A small quantity was sufficient to cause solidification of styrene in the course of a week at room temperature. Lawson<sup>67</sup> heated styrene in solvents which had previously been treated with ozone.

**Photocatalysis.** Ordinary light accelerates the polymerization of styrene. Blyth and Hofmann<sup>68</sup> found that exposure of the liquid to light in glass tubes caused thickening. Lemoine<sup>69</sup> noticed that a sample, which was probably impure, polymerized slowly in the dark. Ultraviolet light<sup>70</sup> is very effective. Taylor and Vernon<sup>71</sup> employed light from a mercury arc and noted that the process has certain characteristics of a chain reaction.<sup>72</sup> One molecule may be activated by absorption of light and react with a second molecule. The new double-molecule, which has an excess of energy, reacts with a third and so on down the line until the initially acquired energy has been dissipated.<sup>73</sup>

<sup>56</sup> H. Staudinger and L. Lautenschlager, *loc. cit.* R. C. Houtz and H. Adkins (*J. A. C. S.*, 1933, 55, 1609), contrary to the conclusions of Staudinger and Lautenschlager, have indicated that peroxides and ozonides are much more active than oxygen as polymerization catalysts. See also R. C. Houtz and H. Adkins, *ibid.*, 1931, 53, 1058.

<sup>57</sup> H. Stobbe and G. Posnjak, *Ann.*, 1909, 371, 259.

<sup>58</sup> I. Ostromislensky, U. S. P. 1,683,404, Sept. 4, 1928, to Naugatuck Chemical Co.; *Chem. Abs.*, 1928, 22, 3893.

<sup>59</sup> W. E. Lawson and L. T. Sandburn, U. S. P. 1,881,282, Oct. 4, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 513. British P. 319,590, 1929; *Brit. Chem. Abs. B*, 1931, 685. French P. 682,126, 1929.

<sup>60</sup> F. Fichter and A. Schnider found benzoyl peroxide to give some resin when exposed to ultraviolet light. *Helv. Chim. Acta*, 1930, 13, 1428; *Brit. Chem. Abs. A*, 1931, 220.

<sup>61</sup> British P. 355,573, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 32. French P. 709,592, 1931, *Chem. Abs.*, 1932, 26, 1300.

<sup>62</sup> H. Staudinger and L. Lautenschlager, *loc. cit.*

<sup>63</sup> I. Ostromislensky, U. S. P. 1,683,404, Sept. 4, 1928; *Chem. Abs.*, 1928, 22, 3893.

<sup>64</sup> S. Natelson, *Ind. Eng. Chem.*, 1933, 25, 1391.

<sup>65</sup> H. J. Barrett, U. S. P. 1,942,531, Jan. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1717.

<sup>66</sup> R. C. Houtz and H. Adkins, *J. A. C. S.*, 1931, 53, 1058.

<sup>67</sup> W. E. Lawson, U. S. P. 1,890,060, Dec. 6, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1639. British P. 319,587, 1929; *Brit. Chem. Abs. B*, 1931, 666. French P. 682,127, 1929.

<sup>68</sup> Blyth and Hofmann, *Ann.*, 1845, 53, 291.

<sup>69</sup> G. Lemoine, *Compt. rend.*, 1897, 125, 530, 1899, 129, 719.

<sup>70</sup> British P. 409,132, 1933, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B*, 1934, 534.

<sup>71</sup> H. S. Taylor and A. A. Vernon, *J. A. C. S.*, 1931, 53, 2527.

<sup>72</sup> Other polymerization reactions have been known to involve a chain mechanism. See, for example, J. B. Couant and C. O. Tongberg, *J. A. C. S.*, 1930, 52, 1659. H. W. Starkweather and G. B. Taylor, *ibid.*, 4708.

<sup>73</sup> H. Stobbe (*Ber.*, 1914, 47, 2701) considered the polymerization of styrene by light to be reversible. He noticed that a solution of polystyrene, after exposure to ultraviolet light, decolorized permanganate, presumably by depolymerization to form styrene. A polystyrene solution which had been kept in the dark did not decolorize permanganate.



In the presence of carbonyl compounds, styrene is readily polymerized in glass (in a few hours with benzophenone and benzanthrone under a 500-watt lamp at 60-70°C.). Apparently traces of activated oxygen play a role in initiating the chain reaction. Antioxidants inhibit the reaction.<sup>74</sup> Exposure to a concentrated electromagnetic field is said to stimulate polymerization of styrene.<sup>75</sup>

**Acid Catalysts.** Acids act as polymerization catalysts. Concentrated sulphuric acid<sup>76</sup> has a very vigorous action. Chromic acid causes rapid formation of a dark brown mass. Lespieau and Deluchat<sup>77</sup> prepared p-divinylbenzene and reported that it polymerized very rapidly to an amorphous powder insoluble in ordinary solvents. Sabetay<sup>78</sup> prepared the same compound avoiding all traces of acid, and found it to be much more stable.<sup>79</sup>

Unless present in very small amounts, acids usually impart a dark color to the resin. However, using about 0.5 per cent hydrochloric acid does not unduly affect the color and a product giving a solution of low viscosity is obtained. The reaction may be carried out at 150°C.<sup>80</sup> Fredenhagen<sup>81</sup> recommended hydrofluoric acid as a catalyst.

Stannic chloride is very active and causes polymerization even at low temperatures. When 3 per cent of this reagent is added to styrene at -3°C., reaction sets in at once and the temperature rises to 80°C. An orange-colored product is formed which is probably a complex containing the catalyst in combination. The color disappears on addition of alcohol.<sup>82</sup> Aluminum chloride,<sup>83</sup> as well as other metallic halides,<sup>84</sup> and phenyldiazonium fluoborate<sup>85</sup> are also active catalysts.

Addition of iodine in solid form<sup>86</sup> causes polymerization but using a solution of iodine<sup>87</sup> largely inhibits this action on account of the formation of iodine compounds. Iodine influences the autoxidation in contact with air.<sup>88</sup> Bromine water causes partial polymerization.<sup>89</sup>

Mercaptans<sup>90</sup> act as resin-forming catalysts especially in the presence of oxygen, a fact which has a bearing on the use of such materials as stench-producers in city gas that contains styrene. Sulphur dioxide<sup>91</sup> in the presence of oxygen or peroxides also has a positive effect on olefins in general, but not as pronounced as mercaptans. The action is explained as the result of the catalytic effect of sulphur trioxide, the latter being formed through oxidation of sulphur dioxide by the peroxides.

**Alkaline Catalysts.** Metallic sodium reacts very slightly with styrene. First a small amount of an orange-colored compound is formed and then polymeriza-

<sup>74</sup> R. Pummerer and H. Kehlen, *Ber.*, 1933, 66, 1107; *Chem. Abs.*, 1933, 27, 6018; *Rubber Chem. Tech.*, 1934, 7, 184; *Chem. Abs.*, 1934, 28, 4628. German P. 576,141, 1933. *Chem. Abs.*, 1933, 27, 3721.

<sup>75</sup> British P. 417,501, Sept. 28, 1934, to Terman A.-G.; *Chem. Abs.*, 1935, 29, 1178

<sup>76</sup> M. Berthelot, *Bull. soc. chim.*, 1866, (2) 6, 296.

<sup>77</sup> R. Lespieau and R. Deluchat, *Compt. rend.*, 1930, 190, 683; *Chem. Abs.*, 1930, 24, 2733.

<sup>78</sup> S. Sabetay, *Compt. rend.*, 1931, 192, 1109; *Chem. Abs.*, 1931, 25, 3973.

<sup>79</sup> 2,4-Dimethyl-3-vinylpyrrol-5-carboxylic acid is easily resinsified by hydriodic or sulphuric acid, the product being of an orange color and insoluble in alkaline solutions. (H. Fischer and B. Walach, *Ber.*, 1925, 58, 2818; *Chem. Abs.*, 1926, 20, 1620) 4'-Hydroxy-9-styrylxanthylium chloride becomes resinous in contact with hydrogen chloride. (H. Atkinson and I. M. Heilbron, *J.C.S.*, 1926, 680)

<sup>80</sup> French P. 712,303, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 3672.

<sup>81</sup> K. Fredenhagen, German P. 524,220, 1930; *Chem. Abs.*, 1931, 25, 3672.

<sup>82</sup> H. Staudinger, K. Frey, P. Garbsch, R. Signer and S. Wehrli, *Ber.*, 1929, 62, 260; *Chem. Abs.*, 1929, 23, 2949.

<sup>83</sup> J. Böeseken and J. Noorduyn, *Rec. trav. chim.*, 1915, 34, 265; *Chem. Abs.*, 1916, 10, 188. C. D. Nenitzescu, D. A. Isacescu and E. N. Ionescu, *Ann.*, 1931, 491, 210; *Chem. Abs.*, 1932, 26, 1257. H. Wieland and E. Dorrer, *Ber.*, 1930, 63, 404; *Brit. Chem. Abs. A.*, 1930, 464.

<sup>84</sup> French P. 761,754, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 4257.

<sup>85</sup> H. A. Bruson, U. S. P. 1,892,101, Dec. 27, 1932, to Resinous Products & Chem. Co., *Chem. Abs.*, 1933, 27, 1993.

<sup>86</sup> M. Berthelot, *Bull. soc. chim.*, 1866, (2) 6, 296.

<sup>87</sup> A. Krakau, *Ber.*, 1878, 11, 1260.

<sup>88</sup> C. Moreu and C. Dufraisse, *Compt. rend.*, 1924, 178, 824; *Chem. Abs.*, 1924, 18, 2635.

<sup>89</sup> J. Read and W. G. Reid, *J.C.S.*, 1928, 1483.

<sup>90</sup> A. L. Ward, C. W. Jordan and W. H. Fulweiler, *Ind Eng Chem.*, 1932, 24, 1238. See also O. Kruber and W. Schade, *Brennstoff-Chem.*, 1933, 14, 124; *Brit. Chem. Abs. B.*, 1933, 418.

<sup>91</sup> H. A. Cassar, *Ind. Eng. Chem.*, 1931, 23, 1132.

tion occurs.<sup>92</sup> Matthews<sup>93</sup> produced a tough resin by allowing styrene to stand in contact with metallic sodium for some time. A solution of sodium in liquid ammonia converted styrene partly to ethylbenzene and partly to resin.<sup>94</sup> Sodium malonic ester<sup>95</sup> causes partial resinification. When styrene is heated in a sealed tube at 100-120°C. with an aqueous solution of sodium bisulphite the polymer is formed together with sodium phenylethylsulphonate.<sup>96</sup> Alkali hydroxides, salts, organic bases or water added to an ethylbenzene solution cause resinification after prolonged heating under a reflux condenser.<sup>97</sup>

Carbonyls of the heavy metals<sup>98</sup> and lead tetraethyl<sup>99</sup> also have been suggested as catalysts.

**Negative Catalysts.** The main substances which have been found to inhibit the polymerization of styrene are sulphur,<sup>100</sup> benzoquinone,<sup>101</sup> trinitrobenzene,<sup>102</sup> anthracene,<sup>103</sup> and phenols such as hydroquinone,<sup>104</sup> cresol and pyrogallol.<sup>105</sup> Inhibitors are useful when it is desired to store styrene for long periods or to distil it. They also prevent the formation of resin from industrial gases containing styrene and other polymerizable hydrocarbons.

### POLYMERIZATION IN SOLUTION

When styrene is dissolved in a solvent and heated, a solution of polystyrene is obtained. If the liquid is a non-solvent for the polymer, the resin precipitates as formed. Berthelot<sup>106</sup> heated styrene and toluene in a sealed tube at 200°C. and obtained a solution of resin. One process of making styrene involves the thermal decomposition of ethylbenzene to give a mixture of styrene and unchanged hydrocarbon.<sup>107</sup> Ostromislensky and Gibbons<sup>108</sup> heated such a solution containing about 40 per cent styrene in the presence of air and obtained a solution of polystyrene which could be used as a lacquer or as an impregnating agent. The resin may be recovered by distilling off the solvent. Steam distillation or heating in a vacuum oven has also been used to free the resin of solvent. In a procedure involving polymerization in solution, Johnston and Keen<sup>109</sup> utilized a combination of spray-drying and steam distillation, atomizing a hot solution containing polystyrene by means of steam at high pressure.

<sup>92</sup> W. Schlenk, J. Appenrodt, A. Michael and A. Thal, *Ber.*, 1914, 47, 473

<sup>93</sup> F. E. Matthews, *British P.* 16,277, 1911, *J.S.C.I.*, 1912, 32, 886

<sup>94</sup> C. B. Wooster and J. F. Ryan, *J.A.C.S.*, 1934, 56, 1133

<sup>95</sup> P. Herman and D. Vorlander, *Abhand. Naturforsch. Ges. Halle*, 1897, 21, 251; *Chem. Zentr.*, 1899, 1, 780

<sup>96</sup> W. v. Miller, *Ann.*, 1877, 189, 340

<sup>97</sup> O. H. Smith, U. S. P. 1,908,549, May 9, 1933, to Naugatuck Chemical Co.; *Chem. Abs.*, 1933, 27, 3726. *British P.* 355,790, 1930, *Chem. Abs.*, 1932, 26, 5580. *French P.* 695,576, 1930, *Chem. Abs.*, 1931, 25, 2749.

<sup>98</sup> O. Ambros and H. Reindel, *German P.* 523,033, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3358. *British P.* 340,004, 1929; *Chem. Abs.*, 1931, 25, 2878.

<sup>99</sup> C. O. Young and S. D. Douglas, U. S. P. 1,775,882, Sept. 16, 1930, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1930, 24, 5308.

<sup>100</sup> A. Krakau, *Ber.*, 1878, 11, 1280.

<sup>101</sup> I. Ostromislensky and M. G. Shepard, U. S. P. 1,550,324, Aug. 18, 1925, to Naugatuck Chemical Co.; *Chem. Abs.*, 1925, 19, 3491. *Canadian P.* 261,327, 1926; *Chem. Abs.*, 1926, 20, 3461.

<sup>102</sup> I. Ostromislensky and M. G. Shepard, U. S. P. 1,550,323, Aug. 18, 1925; *Chem. Abs.*, 1925, 19, 3491.

<sup>103</sup> N. A. Milas, *Proc. Nat. Acad. Sci.*, 1928, 14, 844; *Chem. Abs.*, 1929, 23, 823.

<sup>104</sup> C. Moureu and C. Dufraisse, *J.S.C.I.*, 1928, 47, 828. H. S. Taylor and A. A. Vernon, *J.A.C.S.*, 1931, 53, 2527.

<sup>105</sup> W. H. Fulweiler, *British P.* 336,456, 1929, to Humphrey & Glasgow, Ltd.; *Chem. Abs.*, 1931, 25, 1976. See also A. L. Ward, C. W. Jordan and W. H. Fulweiler, *Ind. Eng. Chem.*, 1932, 24, 1238.

<sup>106</sup> M. Berthelot, *Bull. soc. chim.*, 1866 (2) 6, 296

<sup>107</sup> I. Ostromislensky and M. G. Shepard, U. S. P. 1,541,175, June 1, 1925, to Naugatuck Chemical Co.; *Chem. Abs.*, 1926, 20, 424. *Canadian P.* 261,324, 1926. *British P.* 232,909, 1926; *Brit. Chem. Abs.*, 1926, 299. *German P.* 476,270, 1924; *Chem. Abs.*, 1929, 23, 3717.

<sup>108</sup> I. Ostromislensky and W. A. Gibbons, U. S. P. 1,855,413, April 26, 1932, to Naugatuck Chem. Co.; *Chem. Abs.*, 1932, 26, 3344. *Canadian P.* 265,328, 1926; *Chem. Abs.*, 1927, 21, 918. *British P.* 243,768, 1924; *Chem. Abs.*, 1927, 21, 593.

<sup>109</sup> W. S. Johnston and A. W. Keen, U. S. P. 1,673,685, June 12, 1928, to Naugatuck Chemical Co.; *Chem. Abs.*, 1928, 22, 2801. *British P.* 292,137, 1928; *Brit. Chem. Abs.*, 1929, 65. *French P.* 651,939, 1928; *Chem. Abs.*, 1929, 23, 3523. *Canadian P.* 283,915, 1928, to Dominion Rubber Co., Ltd.; *Chem. Abs.*, 1929, 23, 611.

Any soluble polymerization catalyst may be added to a solution of styrene. Lawson and Sandborn<sup>110</sup> used benzoyl peroxide. Heating 3900 grams of a 21.7 per cent solution of styrene in ethylbenzene containing 8 g. of benzoyl peroxide for 5 hours at 115-120°C. resulted in polymerizing 56 per cent of the styrene. A solution containing a catalyst is best handled by first heating a small portion until the exothermic reaction ceases and then adding the remainder of the solution gradually. A special apparatus<sup>111</sup> for this kind of work consists of a lower vessel containing the solution and an upper compensating chamber into which the liquid distills when the reaction starts and from which it returns gradually after cessation of the initial reaction.

Smith<sup>112</sup> added a small amount of an alkali hydroxide, an organic base or water to an ethylbenzene solution of styrene. Heating under reflux for 72 hours gave a tough, nonfriable resin.

In order to accelerate subsequent polymerization under heat and pressure, Lawson<sup>113</sup> subjected a solution of styrene to ozone treatment for a period of 5 hours. This procedure may become a continuous process<sup>114</sup> for the preparation of polystyrene by passing the ozone-treated solution, or any solution containing a catalyst such as benzoyl peroxide, slowly under pressure through a lead-lined tube heated at about 117°C. Passage of a 45 per cent solution in ethylbenzene (to which 3 per cent of benzoyl peroxide had been added) under a pressure of 200 pounds per square inch, and at a flow-rate of 200 cc. per hour, resulted in polymerization of 65 per cent of the styrene.<sup>115</sup>

Vinylnaphthalene<sup>116</sup> also may be polymerized to a resin. This may be done by heating the compound at 300°C., or by dissolving it in a solvent and heating at a lower temperature in presence of a catalyst. The polymer is light colored and suitable for lacquers or molding compositions. Furylethylene,<sup>117</sup> another compound related to styrene, when heated for 6 hours under pressure at 180°C. with 1 per cent of benzoyl peroxide, yields a light red syrup soluble in toluene. The polymerization can be carried out in solution and a lacquer obtained directly. Five per cent of blown linseed oil may be added as a catalyst. Polyfurylethylene forms films which dry tack-free in 8 hours and hard in 24 hours. Unlike polystyrene, it is compatible with nitrocellulose. The resinification of furylethylene is very sensitive to antioxidants, phenols (hydroquinone in particular) largely inhibiting the reaction.<sup>118</sup> Furylbromoethylene resinifies quite easily, and when exposed in a thick layer to air it changes to a solid.<sup>119</sup>

#### COMPLEXES BY CO-POLYMERIZATION

A mixture of two or more polymerizable substances, when subjected to appropriate conditions, may form a complex resin having properties different from a

<sup>110</sup> W. E. Lawson and L. T. Sandborn, U. S. P. 1,881,282, Oct. 4, 1932, to E. I. du Pont de Nemours & Co., *Chem. Abs.*, 1933, 27, 513. British P. 319,590, 1929; *Brit. Chem. Abs. B*, 1931, 685. French P. 682,126, 1929.

<sup>111</sup> British P. 331,265, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 116

<sup>112</sup> O. H. Smith, British P. 355,790, 1930, to Naugatuck Chemical Co.; *Brit. Chem. Abs. B*, 1932, 72. French P. 695,576, 1930; *Chem. Abs.*, 1931, 25, 2740.

<sup>113</sup> W. E. Lawson, U. S. P. 1,890,080, Dec. 6, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1639. British P. 319,537, 1929; *Brit. Chem. Abs. B*, 1931, 666. French P. 682,127, 1929

<sup>114</sup> For other continuous process apparatus see French P. 723,440, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4065. British P. 381,693, 1931; *Brit. Chem. Abs. B*, 1933, 158

<sup>115</sup> W. E. Lawson, U. S. P. 1,867,014, July 12, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 4611. British P. 319,588, 1929; *Brit. Chem. Abs. B*, 1931, 666. French P. 682,128, 1929.

<sup>116</sup> British P. 355,032, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1931, 1004. See also W. E. Lawson, U. S. P. 1,982,076, Dec. 4, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 526.

<sup>117</sup> B. E. Sorenson, U. S. P. 1,911,722, May 30, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 3952. British P. 349,442, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1931, 728. See Chapter 24.

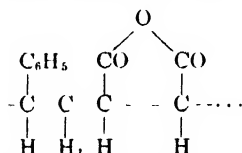
<sup>118</sup> C. Moureu, C. Dufraisse and J. R. Johnson, *Bull. soc. chim.*, 1923, (4) 43, 586; *Brit. Chem. Abs. B*, 1923, 718.

<sup>119</sup> C. Moureu, C. Dufraisse and J. R. Johnson, *Ann. chim.*, 1927, 7, 14; *Chem. Abs.*, 1927, 21, 2896.

simple mixture of the two polymers. A mixed-chain polymeric molecule is formed and the reaction is designated co-polymerization. The type and proportions of the different materials may be varied in any way desired, so that the number of possible co-polymers is very large. Styrene may be polymerized in the presence of vinyl chloride,<sup>120</sup> vinyl ethers and esters,<sup>121</sup> acrylic esters, acrylonitrile<sup>122</sup> and acrylyl chloride,<sup>123</sup> 2-chloro-1,3-butadiene,<sup>124</sup> unsaturated ketones<sup>125</sup> or unsaturated  $\alpha$ ,  $\beta$ -dicarboxylic acids<sup>126</sup> to yield resins. In the case of ketones, the resin formed is less brittle than the styrene resin and more soluble in benzene than a resin from the corresponding ketone alone.<sup>127</sup>

#### COMPLEXES BY HETEROPOLYMERIZATION

When a complex is formed from a mixture containing one polymerizable substance, such as styrene, and another that is not ordinarily capable by itself of polymerizing, such as maleic anhydride or cyclohexanol, the reaction is one of heteropolymerization.<sup>128</sup> Voss and Dickhauser,<sup>129</sup> by heating a mixture of 120 parts maleic anhydride and 105 parts styrene on a water bath, obtained an exothermic reaction which yielded a hard, homogeneous mass. The product from this reaction has properties different from polystyrene: it is insoluble in benzene but soluble in acetone and aqueous alkalis. The properties may be varied by changing the proportions of reactants. The constitution of the resin<sup>130</sup> may be represented as a long chain or ring of alternate maleic anhydride and styrene groups.



A solution of this heteropolymer in aqueous ammonia is recommended as a textile dressing. Fabrics are impregnated with the solution, and dried in an oven in order to eliminate the ammonia and to render the resin resistant to washing and soaping.<sup>131</sup> Color lakes for varnishes are improved as regards freedom from bronze luster when precipitated in the presence of an aqueous solution of alkali salts of styrene-maleic acid.<sup>132</sup>

Styrene-maleic anhydride may be converted into esters, salts or amides by reac-

<sup>120</sup> British P. 313,569, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1236. French P. 676,424, 1929; *Chem. Abs.*, 1930, 24, 2846.

<sup>121</sup> British P. 357,173, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1931, 1107. French P. 725,844, 1931; *Chem. Abs.*, 1932, 26, 4827. See Chapter 51.

<sup>122</sup> British P. 371,396, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 688. See Chapter 53.

<sup>123</sup> British P. 351,508, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3138.

<sup>124</sup> W. E. Hugh, British P. 345,939, 1929, to Standard Telephones & Cables, Ltd.; *Chem. Abs.*, 1932, 26, 2085. French P. 707,692, 1930, to Le Material telephonique (soc anon); *Chem. Abs.*, 1931, 25, 2418. See Chapter 8.

<sup>125</sup> British P. 399,232, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1881. French P. 734,985, 1932; *Chem. Abs.*, 1933, 27, 1221. See also German P. 599,058, 1934; *Chem. Abs.*, 1934, 28, 6004. See Chapter 25.

<sup>126</sup> A. Voss and L. Berlin, German P. 598,732, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6004.

<sup>127</sup> K. Meisenburg, W. Bock and D. Bächle, U. S. P. 1,937,063, Nov. 28, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1207.

<sup>128</sup> T. Wagner-Jauregg, *Ber.*, 1930, 63, 3213; *Chem. Abs.*, 1931, 25, 2418.

<sup>129</sup> A. Voss and E. Dickhauser, German P. 540,101, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1813. British P. 376,479, 1931; *Brit. Chem. Abs.* B, 1932, 948. French P. 719,145, 1931.

<sup>130</sup> See Chapter 40 for another structure.

<sup>131</sup> A. Voss, K. Joachim, E. Dickhäuser and H. Geier, German P. 553,174, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4794. French P. 728,712, 1931; *Chem. Abs.*, 1932, 26, 6160. See also German P. 571,665, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4419.

<sup>132</sup> British P. 359,643, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 427. See also British P. 369,915, 1930; *Chem. Abs.*, 1933, 27, 3046. Cf. H. Reindel and A. Ohmer, U. S. P. 1,974,510, Sept. 25, 1934, to Gen. Aniline Works; *Chem. Abs.*, 1934, 28, 7554.

tions affecting the carboxyl-groups of the polymer. These may be of value as germicides or antiparasitic adhesive layers and also in dyeing.<sup>133</sup> Polystyrene can also be used as a binding agent in color printing.<sup>134</sup>

Treatment with glycerol gives an ester which is insoluble in alkalis. The glyceride may also be formed by heating a mixture of maleic anhydride, styrene and glycerol in an autoclave.<sup>135</sup> Wagner-Jauregg<sup>136</sup> found that styrene and dimethyl maleate reacted to form a white, amorphous powder. Polymers of styrene, vinyl ethers and ketones condensed with aldehydes have been suggested for insulators.<sup>137</sup>

Cyclohexanol is not a solvent for polystyrene.<sup>138</sup> When a solution of styrene in cyclohexanol is heated in absence of a catalyst a turbid product resembling paraffin wax results.<sup>139</sup> Clear, colorless masses suitable for molding are obtained by including acetic anhydride or a plasticizer such as camphor or ethylacetanilide in the composition. Styrene polymerized with 5-10 per cent of a chlorobiphenyl yields a harder, less inflammable and more easily molded resin.<sup>140</sup>

### POLYMERIZATION OF EMULSIONS

When styrene is emulsified with water and heated, a latex is formed. This method of forming the resin has certain advantages. The reaction may be carried out at relatively low temperatures and the product is easily purified and very light in color.

Styrene forms a fairly stable emulsion when shaken with water containing a small amount of ammonium oleate. Heating this emulsion at 140°C. under pressure for 24 hours forms a latex which may be coagulated in the same way as rubber latex. Addition of methanol causes the polystyrene to separate in a finely divided form which is easy to wash and dry.<sup>141</sup> Styrene also may be emulsified by means of saponin, sulphonates or albuminous substances. Heating an emulsion made with milk for 10 days at 60°C. causes transformation of the styrene.<sup>142</sup> Latex formation is accelerated by addition of hydrogen peroxide.<sup>143</sup> Prior to coagulation by precipitating agents, all volatile impurities may be removed by passing steam or inert gases through the dispersion.<sup>143</sup> In this way a colorless polymer is obtained.

Co-polymerization may also be carried out with the reactants in an emulsified condition. Butadiene or isoprene and styrene form a co-polymer which is rubber-like.<sup>144</sup> For example, 2 parts of butadiene and 1 part of styrene emulsified with sodium stearate are maintained at 60°C. for several days to yield a latex which is then coagulated and the product milled with carbon black. Vulcanization of the composition gives a pliable rubber. Diethylaminoethyloleamide hydrochloride

<sup>133</sup> French P. 763,027, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5190.

<sup>134</sup> E. Knebel and Hermann Winkler, German P. 592,661, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3595.

<sup>135</sup> A. Voss and E. Dickhäuser, German P. 544,326, 1930, addn. to 540,101; *Chem. Abs.*, 1932, 26, 2609; British P. 376,481, 1931, addn. to 376,479; *Brit. Chem. Abs. B*, 1932, 948.

<sup>136</sup> T. Wagner-Jauregg, *loc. cit.*

<sup>137</sup> British P. 408,225, 1934, to Helge Rost.; *Chem. Abs.*, 1934, 28, 5555.

<sup>138</sup> G. S. Whitby, *Fourth Colloid Symposium Monograph*, 1926, 203; *Chem. Abs.*, 1927, 21, 3293.

<sup>139</sup> E. Laage, German P. 547,383, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3518; British P. 341,420, 1929, *Chem. Abs.*, 1931, 25, 4673.

<sup>140</sup> R. Müller, German P. 398,279, 1934, to Allgem. Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 5472.

<sup>141</sup> I. Ostromislensky, U. S. P. 1,676,281, July 10, 1928, to Naugatuck Chemical Co.; *Chem. Abs.*, 1928, 22, 3171. British P. 233,649, 1924; *Brit. Chem. Abs. B*, 1926, 451. Canadian P. 265,326, 1926; *Chem. Abs.*, 1927, 21, 918. German P. 491,727, 1924.

<sup>142</sup> K. Meisenburg, German P. 573,648, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4430. British P. 307,936, 1929; *Chem. Abs.*, 1930, 24, 253.

<sup>143</sup> British P. 355,573, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 57. French P. 709,592, 1931; *Chem. Abs.*, 1932, 26, 1300.

<sup>144</sup> British P. 365,217, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 519. French P. 713,999, 1931; *Chem. Abs.*, 1932, 26, 1620.

<sup>145</sup> E. Tschunkur and W. Bock, U. S. P. 1,938,731, Dec. 12, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1574. German P. 532,456, 1929; *Chem. Abs.*, 1932, 26, 337. British P. 339,255, 1929; *Chem. Abs.*, 1931, 25, 2598. French P. 699,154, 1930; *Chem. Abs.*, 1931, 25, 3521.

is recommended as an emulsifying agent. Divinylbenzene or  $\alpha$ -methylstyrene<sup>141</sup> may be substituted for styrene; or vinylnaphthalene<sup>142</sup> may be used. If the polymerization is stopped when about 20 per cent of the diolefin is unconverted the product has maximum solubility in benzene, but if the process is carried to completion poor solubility results.<sup>147</sup> The addition of a chlorine compound, such as carbon tetrachloride, ethylene dichloride, hexachloroethane or sodium trichloroacetate, to the emulsified mixture of styrene and diolefin causes an increased yield and a more plastic product.<sup>148</sup>

Ethyl acrylate (see Chapter 53) and styrene may be emulsified by means of sodium isopropyl-naphthalenesulphonate, and the emulsion on the addition of hydrogen peroxide and heating at 70-90°C. yields a co-polymer which may be formed into rubber-like threads and films.<sup>149</sup> Threads of artificial silk are produced by spinning a solution of a resin into a coagulating bath to produce a strongly swollen thread which is then stretched. Solutions of polymers of styrene, vinyl alcohol, vinyl acetate, vinyl chloroacetate, vinylamine or vinyl methyl ketone can be thus used; or, heteropolymers of these with maleic anhydride.<sup>150</sup>

### POLYMERIZATION UNDER PRESSURE

The velocity of polymerization of styrene increases with increasing pressures, and at high pressures, a lower temperature will bring about resinification.<sup>151</sup> Pressures as high as 12,000 atmospheres have been suggested, using a pressure vessel consisting of a block of chrome-vanadium steel 6 inches in diameter with a 1-inch hole drilled in it.<sup>152</sup>

### POLYSTYRENE COATINGS

On account of its solubility in cheap hydrocarbon solvents,<sup>153</sup> its toughness and light color, polystyrene offers excellent possibilities as a film-forming material.<sup>154</sup> Suggested uses to which the coatings are adapted are as clear metal lacquers and as bases for white or pale-colored enamels which do not darken in the light. The lacquers are quick-drying and even when baked for a long time the films do not become insoluble. They are resistant to water, sea water, and moderately strong acids and alkalis, but are not quite as tough as nitrocellulose films.

Exposure tests of polystyrene coatings show that plasticizers are advisable. Photomicrographs after 60 days of exposure of a coating formed from a 33 per cent solution of polystyrene in toluol showed fine cracks. A similar composition to which had been added 5 per cent of diphenyl phthalate gave high gloss and no

<sup>145</sup> E. Tschunkur and W. Bock, U. S. P. 1,938,730, Dec. 12, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1574. German P. 570,980, 1933; *Chem. Abs.*, 1933, 27, 4441. British P. 342,314, 1929, (addn. to 339,255), to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4443. French P. 701,102, 1930. *Chem. Abs.*, 1931, 25, 3876. See also German P. 588,785, 1933, addn. to 570,980; *Chem. Abs.*, 1934, 28, 2205.

<sup>146</sup> K. Meisenburg and W. Bock, U. S. P. 1,938,751, Dec. 12, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1 34, 28, 1574. German P. 573,568, 1933; *Chem. Abs.*, 1933, 27, 4441. British P. 358,877, 1930, addn. to 339,255; *Chem. Abs.*, 1932, 26, 6183.

<sup>147</sup> British P. 364,089, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1932, 494.

<sup>148</sup> W. Bock and E. Tschunkur, German P. 532,271, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 337. British P. 349,499, 1930; *Brit. Chem. Abs.*, B, 1931, 730.

<sup>149</sup> British P. 358,534, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1932, 172. French P. 710,901, 1931; *Chem. Abs.*, 1932, 26, 1830.

<sup>150</sup> British P. 387,978, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4672.

<sup>151</sup> G. Tammann and A. Pape, *Z. anorg. Chem.*, 1931, 200, 113; *Brit. Chem. Abs.*, A, 1931, 1239.

<sup>152</sup> P. W. Bridgman and J. B. Conant, U. S. P. 1,952,116, Mar. 27, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3415. French P. 699,555, 1930; *Chem. Abs.*, 1931, 25, 3358. See also British P. 365,102, 1932, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 1643.

<sup>153</sup> On thixotropic effects noted in polystyrene solutions see R. O. Herzog, O. Kratky and E. Peterlin, *Trans. Faraday Soc.*, 1933, 29 (1), 80; *Chem. Abs.*, 1933, 27, 1802.

<sup>154</sup> A lacquer composed of polystyrene dissolved in a hydrocarbon solvent was proposed by E. Haslinger, Swiss P. 155,462, 1931; *Chem. Abs.*, 1933, 27, 1218.

checking, indicating the superiority of the plasticized film.<sup>155</sup> Some of the softer Aroclors<sup>156</sup> are suitable plasticizers. Dibutyl phthalate, triphenyl phosphate and tricresyl phosphate decrease the water-resistance of polystyrene in the order named but give clear films. Resin oils have also been suggested for this purpose.<sup>157</sup> Jaeger recommended esters of keto-aromatic acids such as methyl benzoylbenzoate,<sup>158</sup> soft substances such as phthalide-phthalic-glyceride,<sup>159</sup> or hexahydro-phthalide and substituted phthalides as plasticizers.<sup>160</sup> About 1 per cent of di-*o*-tolylguanidine added to polystyrene solutions acts as a protective agent to prevent checking of coatings.<sup>161</sup>

A difficulty encountered when using a solution of polystyrene as a spraying lacquer is cobweb formation. This is the tendency of a solution to come from the spray-gun in the form of long thread-like filaments. It generally occurs when the solution is too viscous or if the air-pressure is too low, and can usually be corrected by thinning the solution or adding other resins and plasticizers. Lawson and Sandborn<sup>162</sup> stated that the product obtained by polymerizing styrene in a solvent and in the presence of a catalyst forms lacquers which do not cobweb. Ethylbenzene is a suitable solvent for use during the resinification, and benzoyl peroxide, the best catalyst. Styrene is heated in the solution at a temperature of 115°C. until polymerized. A lacquer which does not cobweb is made from 175 parts of polystyrene thus prepared, 50 parts tricresyl phosphate and 500 parts solvent consisting of 15 per cent benzene, 45 per cent toluene and 40 per cent xylene.

When polystyrene is dissolved in carbon tetrachloride and chlorine passed through the solution in the presence of ferric or aluminum chloride at ordinary temperatures and in the dark, a chlorinated substance capable of being sprayed is obtained.<sup>163</sup> Resins having the highest chlorine content show the lowest viscosity and highest melting point.<sup>164</sup>

Lawson<sup>165</sup> used polystyrene plasticized by means of tricresyl phosphate, dibutyl phthalate, glycerol dibenzyl ether, butyl stearate or dixylylethane as a coating for glass, wood<sup>166</sup> or metal. Such a lacquer is composed of a mixture of polystyrene 17.8 parts by weight, dibutyl phthalate 4.5 (or tricresyl phosphate 3.6), ethyl acetate 20, toluol 30, xylol 20 and butyl acetate 30.<sup>167</sup> This lacquer is suitable for waterproofing shotgun shells.<sup>168</sup> Lacquers containing polystyrene plasticized with 50 per cent of diphenyl phthalate have been recommended as clear top varnishes on lithographed metal advertising signs to prevent chalking and fading of certain colors,<sup>169</sup> or as vehicles for luminous pigments.<sup>170</sup> A film of polystyrene applied to

<sup>155</sup> H. A. Gardner, *Circ. Am. Paint & Varnish Mfrs. Assoc.*, 1932, 410.

<sup>156</sup> See Chapter 56.

<sup>157</sup> E. Laage, German P. 560,372, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1217.

<sup>158</sup> A. O. Jaeger, British P. 359,164, 1930, to Selden Co.; *Brit. Chem. Abs. B*, 1932, 118.

<sup>159</sup> A. O. Jaeger, U. S. P. 1,860,098, May 24, 1932, to Selden Co.; *Chem. Abs.*, 1932, 26, 3945.

<sup>160</sup> A. O. Jaeger, U. S. P. 1,892,784, Jan. 3, 1933, to Selden Co.; *Chem. Abs.*, 1933, 27, 2298.

<sup>161</sup> H. J. Barrett and E. F. Izard, U. S. P. 1,896,504, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 2830.

<sup>162</sup> W. E. Lawson and L. T. Sandborn, U. S. P. 1,881,282, Oct. 4, 1932, to E. I. du Pont de Nemours & Co.; British P. 319,590, 1929; *Brit. Chem. Abs. B*, 1931, 685. French P. 682,126, 1929. See also U. S. P. 1,975,959, Oct. 9, 1934; *Chem. Abs.*, 1934, 28, 7562.

<sup>163</sup> British P. 364,873, 1931, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1932, 494.

<sup>164</sup> Chlorinated polystyrene has been recommended as a flux for soft soldering. H. B. Dykstra, U. S. P. 1,800,445, Apr. 14, 1931, to Grasselli Chemical Co.; *Chem. Abs.*, 1931, 25, 3308.

<sup>165</sup> W. E. Lawson, U. S. P. 1,792,102, Feb. 10, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 2012. British P. 311,700, 1929; *Brit. Chem. Abs. B*, 1930, 872.

<sup>166</sup> Hardwood coated with a polystyrene resin has been used in electrical line insulators. H. Rost, U. S. P. 1,991,700, Feb. 19, 1935; *Chem. Abs.*, 1935, 29, 2261.

<sup>167</sup> W. E. Lawson, Canadian P. 312,341, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1931, 25, 4138.

<sup>168</sup> C. E. Burke and W. E. Lawson, U. S. P. 1,862,565, June 14, 1932, to E. I. du Pont de Nemours & Co.; British P. 315,228, 1928; *Chem. Abs.*, 1930, 24, 1742.

<sup>169</sup> H. A. Gardner, *Circ., Amer. Paint & Varnish Mfrs. Assoc.*, 1933, 427; *Brit. Chem. Abs. B*, 1933, 1068.

<sup>170</sup> A. W. Van Heuckeroth, *Circ., Amer. Paint & Varnish Mfrs. Assoc.*, 1933, 440; *Chem. Abs.*, 1933, 27, 4425. Luminescent pigments can be incorporated in polymerized vinylanthralene and vinyltetrahydronaphthalene, as well as in polystyrene. British P. 400,068, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2203; French P. 731,709, 1933; *Chem. Abs.*, 1934, 28, 917.

hardened synthetic resins serves as an intermediate layer for metallic coatings.<sup>171</sup> Plasticized with aryl phosphates or phthalic esters, polystyrene can be used for impregnating fabrics,<sup>172</sup> or for waterproofing articles made of cellulose esters.<sup>173</sup> Phthalide and its derivatives serve as plasticizers for styrene resin.<sup>174</sup> Solutions of polystyrene or hydrogenated polystyrene may be used to stiffen textile fabrics, felt, straw or asbestos fibers and render them less liable to spot with water.<sup>175</sup> Cloth impregnated with a solution of polystyrene or other vinyl resin is also satisfactory for containers.<sup>176</sup> Electrical conductors can be provided with inorganic insulation by applying a coating of lead borate and over this a thin film of an alkyd resin or polystyrene. The resin film permits the conductor to be wound into coils<sup>176a</sup> and is subsequently volatilized by heating for 2 hours at 380-400°C.

In making surfaces for recording sound, metal or paper can be coated with a solution of polystyrene in monomeric styrene. After the coating is applied polymerization is completed by heating at 60°C. using benzoyl peroxide as catalyst. Hardness and elasticity are altered by incorporating paraffin.<sup>177</sup>

Polystyrene is not compatible with cellulose esters or ethers, polyvinyl acetate or Amberols, giving neither clear solutions nor clear films with these materials. However, polymerization of styrene in the presence of cellulose derivatives in solution yields a homogeneous resin suitable for coating.<sup>178</sup> Cellulose ester products, such as fountain-pens or screw caps, are coated with a film of polystyrene or its homologues to make them resistant to water, acids and alkalis.<sup>179</sup> Polystyrene is compatible with Aroclors, Cumar, ester gum and some other resins. Lacquers may be prepared by mixing solutions of polystyrene with solutions of rosin, dammar, linseed-phthalic-glyceride or methyl tetrahydroabietate.<sup>180</sup> These resins increase the adhesion.

The adhesion of coatings of polystyrene is also improved by the addition of 10-25 per cent of cumarone resin. If a chlorinated resin, such as an Aroclor, is used to the extent of about 40 per cent with polystyrene, a notably fire-resistant coating results. One composition containing polystyrene, cumarone resin and tricresyl phosphate has been used advantageously in the finishing of terrazzo floors.<sup>181</sup> Disadvantages of the use of a volatile solvent are avoided by coating or impregnating articles with monomeric styrene or a solution of polystyrene in styrene, followed by heat-treatment.<sup>182</sup> A varnish containing polystyrene, Cumar and a softener gives a film with little tendency to check.<sup>183</sup>

Walsh and Caprio<sup>184</sup> used styrene and other vinyl compounds in cellulose ester plastics. They prepared solutions containing styrene in an unpolymerized, partially polymerized<sup>185</sup> and highly polymerized form<sup>186</sup> to which were added cellulose

<sup>171</sup> British P. 377,556, 1930, to International General Elec. Co., Inc.; *Chem. Abs.*, 1933, 27, 3350.

<sup>172</sup> British P. 366,461, 1929, to Celluloid Corp.; *Chem. Abs.*, 1933, 27, 3096.

<sup>173</sup> British P. 402,877, 1932, to Celluloid Corp.; *Brit. Chem. Abs. B.*, 1934, 189.

<sup>174</sup> A. O. Jaeger, U. S. P. 1,941,474, Jan. 2, 1934, to Selden Co.; *Chem. Abs.*, 1934, 28, 1880.

<sup>175</sup> British P. 367,126, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 418. French P. 709,141, 1931; *Chem. Abs.*, 1932, 26, 1135.

<sup>176</sup> H. Prieaux, G. Pegnet, P. Degardin and E. Jarny, French P. 764,479, 1934; *Chem. Abs.*, 1934, 28, 5944.

<sup>176a</sup> A. G. Hovey, British P. 380,426, 1932, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 5125.

<sup>177</sup> British P. 413,843, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1935, 29, 256.

<sup>178</sup> W. E. Lawson and L. T. Sandborn, U. S. P. 1,957,959, Oct. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 7562.

<sup>179</sup> British P. 402,877, 1933, to Celluloid Corp.; *Chem. Abs.*, 1934, 28, 2902.

<sup>180</sup> British P. 375,320, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 807; French P. 724,598, 1931; *Chem. Abs.*, 1932, 26, 5220.

<sup>181</sup> Carleton Ellis, *Ind. Eng. Chem.*, 1933, 25, 129.

<sup>182</sup> British P. 401,500, 1932, to International General Elec. Co., Inc.; *Brit. Chem. Abs. B.*, 1934, 157.

<sup>183</sup> O. H. Smith, U. S. P. 1,975,179, Oct. 2, 1934, to Naugatuck Chem. Co.; *Chem. Abs.*, 1934, 28, 7562.

<sup>184</sup> J. F. Walsh and A. F. Caprio, British P. 308,657, 1928, to Celluloid Corp.; *Chem. Abs.*, 1930, 24, 499.

<sup>185</sup> J. F. Walsh and A. F. Caprio, British P. 335,582, 1928; *Chem. Abs.*, 1930, 24, 1672.

<sup>186</sup> J. F. Walsh and A. F. Caprio, British P. 308,658, 1928; *Chem. Abs.*, 1930, 24, 499.



esters, plasticizers and other resins. When using unpolymerized styrene a catalyst such as benzoyl peroxide is introduced and the solution subjected to light and heat. The solutions are used as lacquers or the solvent is evaporated and the plastic worked up into shaped articles.<sup>107</sup> A composition consisting of 1 part cellulose acetate or butyrate, 2 parts polystyrene, 1 part p-toluenesulphonamide, 3 parts kieselguhr and 1 part chlorobenzene, homogenized in a kneading apparatus at 110-120°C., can be made into oilcloth by rolling on to a cloth web.<sup>108</sup>

Polystyrene is insoluble in drying oils but this is not true of the polymer from divinylbenzene. Dykstra<sup>109</sup> suggested a varnish which contains polymerized divinylbenzene, raw tung or linseed oil and cobalt linoleate in a solvent. A coating forms flexible films when dry. Vinylacetylene, vinylanthracene and butadiene hydrocarbons have also been recommended for use in lacquers by polymerizing them in the presence of esters of drying oil acids.<sup>100</sup>

Another suggested use for polystyrene in solution is in lubricating oils.<sup>101</sup> It is reported to improve the lubricating properties of the oil and increase the viscosity.<sup>102</sup> Alternatively, styrene may be added to the oil and polymerized in solution by heating. Hydrogenation renders the polymer more resistant to heat.<sup>103</sup> Solid lubricating greases are also said to be improved by addition of a small amount of polymerized styrene, hexene or turpentine, or hydrogenated rubber.<sup>104</sup>

### MOLDED PRODUCTS

Polystyrene may be readily molded under heat and pressure, preferably at a high temperature as this appears to eliminate internal strains and renders the article less likely to crack on aging.<sup>105</sup> A temperature of 150-190°C. and a pressure of 1000 pounds per square inch are recommended. Curing does not occur and the molded pieces are permanently thermoplastic and soluble. Moldings have remarkably high shock-resistance and are stronger than phenol resins. Their insulating power is highest of any available synthetic resin, higher even than shellac. A particular advantage of polystyrene is the low shrinkage that occurs on cooling; a commercial product has a shrinkage of 0.002 inches per linear inch of molding. These qualities are suggestive of the possible fields for utilization of the plastic.<sup>106</sup>

Strips and bars may be formed by extrusion under pressure of the heat-softened resin through an orifice of suitable size. By passing a wire through the extrusion apparatus, a tubular coating is formed on the surface of the metal (see Fig. 56). This device may be applied to the manufacture of insulated cables.<sup>107</sup> A related process<sup>108</sup> serves for the production of threads or films. In this case the addition of solvents and plasticizers to the polystyrene is recommended.

<sup>107</sup> See also British P. 409,132 and 409,582, 1933, to British Celanese, Ltd.; *Brit. Chem. Abs. B.* 1934, 534, 591.

<sup>108</sup> British P. 386,116, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2051.

<sup>109</sup> H. B. Dykstra, U. S. P. 1,811,078, June 23, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 5049. British P. 374,113, 1931; *Brit. Chem. Abs. B.*, 1932, 778.

<sup>100</sup> O. Jordan, H. Hopff and E. Kuhn, German P. 588,308, 1933, to I. G. Farbenind. A.-G.; addn. to German P. 580,234 (*Chem. Abs.*, 1933, 27, 4943); *Chem. Abs.*, 1934, 28, 1558.

<sup>101</sup> C. Wulff, E. Moll and W. Breuers, German P. 557,306, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 410. British P. 379,717, 1931; *Brit. Chem. Abs. B.*, 1932, 971. French P. 718,506, 1911, *Chem. Abs.*, 1932, 26, 3102.

<sup>102</sup> British P. 411,893, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1934, 749.

<sup>103</sup> French P. 760,861, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 4220.

<sup>104</sup> British P. 401,295, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1934, 184. French P. 42,897, 1933, addn. to 740,407; *Chem. Abs.*, 1934, 28, 1526.

<sup>105</sup> I. Ostromslensky suggested an annealing treatment by heating the moldings for 3 to 24 hours in an oven at 100°C. in order to prevent cracking. U. S. P. 1,883,402, Sept. 4, 1928, *Chem. Abs.*, 1928, 22, 3898.

<sup>106</sup> For mechanical, physical and electrical properties of styrene plastic see compilation in *Chem. Met. Eng.*, 1932, 39, 637.

<sup>107</sup> E. Studd and U. Meyer, U. S. P. 1,992,678, Feb. 26, 1935, to Norddeutsche Seekabelwerke A.-G.; *Chem. Abs.*, 1935, 29, 2629. British P. 419,900, Oct. 16, 1933; *Brit. Chem. Abs. B.*, 1935, 111.

<sup>108</sup> British P. 419,826, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1935, 111.

Small objects are readily formed by injection molding,<sup>100</sup> the plastic being particularly adapted for this method.<sup>200</sup> The resin is heated until plastic and is then forced into a mold where it cools and hardens.<sup>201</sup> Threads, ribbons and sheets can be made by drawing polystyrene at a high temperature.<sup>202</sup>

An advantage of polystyrene as a molding material is that, like shellac, there is no waste in the process. Scraps and broken pieces may be reground and used over again. Clear masses may be formed from small pieces of unfilled material and from those containing bubbles, by adding 5 to 20 per cent of styrene and heating the mixture under a reflux condenser for 3 to 8 hours. Also small pieces may be cemented together. In working up scraps and shavings containing fillers, a fairly

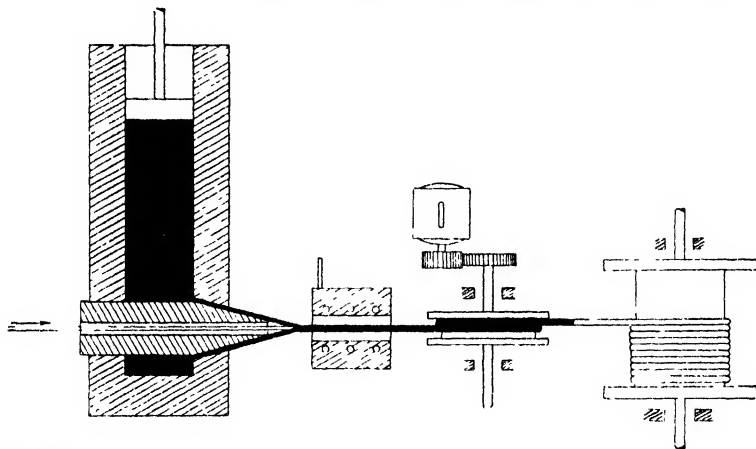


FIG. 56.—Extrusion Apparatus for Coating Wire with Polystyrene Resins. (E. Studt and U. Meyer.)

dilute solution in styrene may be prepared and the insoluble matter allowed to settle.<sup>203</sup>

Posner formed objects by spraying concentrated solutions of polyvinyl compounds into molds.<sup>204</sup> Dentures are made which contain a very tough polymer from which all unpolymerized styrene has been removed, together with fillers and plasticizers.<sup>205</sup> Another type of molding is made by impregnating fibrous material with an aqueous dispersion of polystyrene.<sup>206</sup> The pulp is allowed to dry and is then pressed into the desired shape. Powdered material such as zinc oxide or finely divided asbestos<sup>207</sup> may be made into a paste with partially polymerized styrene and heated to complete the reaction before pressing. The co-polymers of

<sup>100</sup> British P. 383,002 and 383,216, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1933, 79.

<sup>200</sup> H. Stadlinger, *Chem.-Ztg.*, 1932, 56, 409, 431; *Chem. Abs.*, 1932, 26, 4419.

<sup>201</sup> British P. 373,995, 1930, to Cellon-Werke Dr. A. Eichenkrun, *Brit. Chem. Abs.* B, 1932, 779.

<sup>202</sup> French P. 762,538, 1934, to Norddeutsche Seekabelwerke A.-G.; *Chem. Abs.*, 1934, 28, 5190.

<sup>203</sup> I. Ostromslensky and M. G. Shepard, U. S. P. 1,633,401, Sept. 4, 1928, to Naugatuck Chem. Co.; *Chem. Abs.*, 1928, 22, 3893.

<sup>204</sup> F. Posner, German P. 540,552, 1929, to Deutsch Legrit-G. m. b. H., Carl Lindstrom, W. Letzel & Co.; *Chem. Abs.*, 1932, 26, 2609.

<sup>205</sup> E. Roberts, U. S. P. 1,825,286, Sept. 29, 1931, to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, 26, 269. French P. 716,953, 1931, *Chem. Abs.*, 1932, 26, 2834. British P. 379,716, 1931; *Brit. Chem. Abs.* B, 1932, 1042. A polystyrene denture is marketed under the name Teppente. F. Schmidt (British P. 376,036, 1930; *Chem. Abs.*, 1933, 27, 3303) has suggested polystyrene plasticized with tricresyl phosphate or phthalic esters as a denture. W. Hengstmann (German P. 581,675, 1932, addn. to 499,676; *Chem. Abs.*, 1934, 28, 1154) formed dental plates from a mixture of cellulose ethers, aliphatic dicarboxylic acids and polystyrene.

<sup>206</sup> W. A. Gibbons, U. S. P. 1,836,021, Dec. 15, 1931, to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, 26, 1135. British P. 372,217, 1931; *Brit. Chem. Abs.* B, 1932, 595.

<sup>207</sup> British P. 345,197, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1931, 598. French P. 701,439, 1930; *Chem. Abs.*, 1931, 25, 4013.

styrene and acrylic esters, vinyl esters and vinyl ketones may be worked in the same manner as that used for the manufacture of celluloid.<sup>200</sup> Hofmann<sup>200</sup> uses co-polymers of various vinyl compounds, combined with fillers and plasticizers, to make sound records.

On account of its high dielectric constant,<sup>210</sup> polystyrene is valuable in electrical insulators and condensers.<sup>211</sup> A sheath of polymerized styrene air-spaced from the conductor has been proposed.<sup>212</sup> Field, Hugh and Parsons<sup>213</sup> prepared a dielectric composed of purified rubber mixed with 40 to 80 per cent of polystyrene and up to 20 per cent of wax. Rubber compounded with polystyrene, gutta-percha and small amounts of water-resistant waxes has been similarly used.<sup>214</sup> Chlorinated naphthalene with about 1 per cent of polystyrene or rubber has also been suggested as an insulating composition.<sup>215</sup> Other material suitable for insulation of submarine cables contains the product of the co-polymerization of styrene and butadiene, dimethylbutadiene or 2-methyl-2,4-dimethylpentadiene.<sup>216</sup> Another type of cable insulation is made by heating a mixture of styrene, dimethylbutadiene and about 15 per cent of wax in an autoclave;<sup>217</sup> also by mixing polystyrene with plasticizers such as tritolyl and triphenyl phosphate, cresol or diphenylpropane.<sup>218</sup> Marble coated with polystyrene has been found suitable for radio insulation.<sup>219</sup>

Benner and Porter<sup>220</sup> proposed polystyrene as a bonding agent for abrasives. Compositions of phenol-aldehyde resin and polystyrene or shellac have also been suggested.<sup>221</sup> Grinding wheels<sup>222</sup> may be built up of segmental blocks united with a cement composed of polystyrene, plaster of Paris and a solvent. Hadnagy and Brouillard<sup>223</sup> made abrasive paper and cloth by bonding the grains of abrasive material with an adhesive containing polystyrol, used either in molten form or in solution.

#### LAMINATED GLASS

Moss<sup>224</sup> used polystyrene and other polymerized vinyl compounds as adhesives for sheets of glass and cellulose esters in safety glass. The product of the reaction between maleic anhydride and castor oil or 1,3-butylene glycol may be mixed with

<sup>200</sup> French P. 728,861, 1931, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 6081.

<sup>200</sup> H. E. Hofmann, British P. 408,969, 1934, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1934, 28, 6004. See also British P. 409,550, 1934, to Consortium für elektrochem. Ind. GmbH; *Chem. Abs.*, 1934, 28, 6259.

<sup>210</sup> The dielectric constant increases with the degree of polymerization. For determination of constants see Gallay, Kolloid-Z., 1931, 57, 1; *Chem. Abs.*, 1932, 26, 387. For data on the use of polystyrene and thin mica layers in insulation see G. F. Daletzky, *J. Tech. Phys. (U. S. S. R.)*, 1931, 1, 293; *Chem. Abs.*, 1933, 27, 5993. Also see N. P. Bogoroditzki, G. F. Daletzki and V. N. Malishev., *ibid.*, 1931, 3, 831; *Chem. Abs.*, 1934, 28, 2810.

<sup>211</sup> British P. 410,807, 1934, to Elektizitats-A.-G. Hydrawerk; *Chem. Abs.*, 1934, 28, 6375.

<sup>212</sup> British P. 392,416, 1933, to Helge Rost; *Chem. Abs.*, 1933, 27, 5447.

<sup>213</sup> M. C. Field, W. E. Hugh and L. G. B. Parsons, British P. 357,624, 1930, to Standard Telephones & Cables Ltd.; *Brit. Chem. Abs. B*, 1931, 1104.

<sup>214</sup> British P. 414,527, to Norddeutsche Seekabelwerke A.G.; *Brit. Chem. Abs. B*, 1934, 898. See also British P. 408,472, 1934; *Chem. Abs.*, 1934, 28, 5556. French P. 760,240, 1934; *Chem. Abs.*, 1934, 28, 3500. British P. 403,502, 1933, to Siemens & Halske A.-G.; *Chem. Abs.*, 1934, 28, 3270. French P. 767,919, 1934; *Chem. Abs.*, 1935, 29, 643.

<sup>215</sup> British P. 387,744, 1933, to International General Elec. Co., Inc.; *Chem. Abs.*, 1933, 27, 5847.

<sup>216</sup> W. E. Hugh, British P. 345,939, 1929, to Standard Telephones & Cables, Ltd.; *Chem. Abs.*, 1932, 26, 2085. French P. 707,692, 1930, to Le Matériel Téléphonique (Soc. anon.), *Chem. Abs.*, 1932, 26, 734.

<sup>217</sup> J. W. Armit, British P. 346,658, 1929, to Imperial Chem. Ind. Ltd.; *Brit. Chem. Abs. B*, 1931, 710.

<sup>218</sup> British P. 407,718, 1934, to Helge Rost.; *Chem. Abs.*, 1934, 28, 5556.

<sup>219</sup> N. P. Bogoroditzki and G. F. Daletzki, *J. Tech. Phys. (U. S. S. R.)*, 1933, 3, 1200; *Chem. Abs.*, 1934, 28, 2810.

<sup>220</sup> R. C. Benner and G. H. Porter, U. S. P. 1,825,771, Oct. 6, 1931, to Carborundum Co.; *Chem. Abs.*, 1932, 26, 574.

<sup>221</sup> F. A. Upper, U. S. P. 1,950,641, Mar. 13, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 3552.

<sup>222</sup> British P. 319,221, 1928, to Carborundum Co.; *Chem. Abs.*, 1930, 24, 2569.

<sup>223</sup> Z. H. Hadnagy and A. Brouillard, British P. 406,581, 1934; *Chem. Abs.*, 1934, 28, 5200.

<sup>224</sup> W. H. Moss, U. S. P. 1,831,462, Nov. 10, 1931, to Celanese Corp. of Amer., *Chem. Abs.*, 1931, 25, 3795. British P. 341,891, 1929; *Chem. Abs.*, 1932, 26, 2533.

polystyrene to improve its adhesion.<sup>226</sup> Polymerized vinyl compounds also may be blended with the nitrocellulose layer of safety glass and tend to lessen the yellowing effect of light.<sup>226</sup>

Transparent layers for use as glass substitutes are made by blocking compositions containing plasticizers and fire retardants and cutting into sheets.<sup>227</sup> Hopkinson<sup>228</sup> suggested a shatter-proof, glass-like product composed of alternate layers of tough polystyrene and the hard, brittle polymer. Styrene polymerized in the presence of sulphur, sulphur chloride or chlorinated hydrocarbons has been recommended for lenses, prisms and other optical elements, also as a cement for these articles.<sup>229</sup>

#### PRODUCTION OF STYRENE

More extended use of polystyrene demands a cheaper source of styrene. So far, no process appears to have been developed which puts the price on a par with that of other leading synthetic resins. Styrene has been made in a number of ways including the pyrolysis of various hydrocarbons, elimination of hydrogen chloride from chloroethylbenzene, dehydration of phenylethyl alcohols, and decarboxylation of cinnamic acid. Homologues of styrene and substituted styrenes have been made by applying these reactions to analogous compounds. Also its synthesis from acetylene has been attempted.

Styrene occurs ready-formed in coal-tar light-oil fractions and in drip-oil of carburetted water gas. It constitutes a nuisance in motor benzol and in various industrial gases on account of its gum-forming tendencies. Removal of this and other gum-formers would be welcomed by manufacturers of gases and might also serve as a source of synthetic resins.

**Styrene From Chlorinated Hydrocarbons.** At present the most satisfactory process for producing styrene starts with ethylbenzene,<sup>230</sup> a hydrocarbon which is conveniently made by passing ethyl chloride into benzene in the presence of aluminum chloride or from ethylene<sup>231</sup> and benzene. Ethylbenzene when chlorinated below 30°C. gives a mixture of  $\alpha$ - and  $\beta$ -chloroethylbenzene. Passage of the chlorinated hydrocarbon, without separation through a nichrome tube heated to 675-700°C. results in splitting out of hydrogen chloride to yield styrene.<sup>232</sup> Instead of utilizing thermal decomposition, chloroethylbenzene may be treated with pyridine at 100-230°C.,<sup>233</sup> with pyridine or dibenzylamine hydrochlorides or with a cyclic tertiary amine.<sup>234</sup>

Smith<sup>235</sup> concentrated the chloroethylbenzene before treatment with pyridine by distilling off the unchanged ethyl benzene through a column. In this way a more

<sup>226</sup> G. Kränzlein, A. Voss and E. Dickhäuser, German P. 547,384, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3633. British P. 367,658, 1931, (addn. to 349,283); *Brit. Chem. Abs. B*, 1932, 423.

<sup>228</sup> A. Bresser, *Chem. Apparat*, 1932, 19, 62; *Chem. Abs.*, 1932, 26, 4929.

<sup>227</sup> British P. 366,077, 1929, to Celluloid Corp., *Chem. Abs.*, 1933, 27, 3047.

<sup>229</sup> E. Hopkinson, U. S. P. 1,777,309, March 4, 1929, to Naugatuck Chemical Co.; *Chem. Abs.*, 1930, 24, 5958.

<sup>230</sup> E. Brüche, German P. 600,945, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 7446.

<sup>231</sup> For details of an efficient method of preparing ethylbenzene from ethylene and benzene see S. Natelson, *Ind. Eng. Chem.*, 1933, 25, 1391.

<sup>232</sup> A. L. Nugey (*Refiner Natural Gasoline Manuf.*, 1932, 11, 547; *Chem. Abs.*, 1933, 27, 2022) stated that ethylene from cracking-still gases is a potential source of raw material from which to make styrene. See also H. Pincass, *Kunststoffe*, 1933, 27, 2317.

<sup>233</sup> O. H. Smith, U. S. P. 1,687,903, Oct. 16, 1929, to Naugatuck Chemical Co.; *Chem. Abs.*, 1929, 23, 156. French P. 657,990, 1928; *Chem. Abs.*, 1929, 23, 4485. British P. 298,152, 1928; *Brit. Chem. Abs. B*, 1930, 276. German P. 562,823, 1928; *Chem. Abs.*, 1933, 27, 1015.

<sup>234</sup> British P. 356,107, 1930, to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, 26, 5579. French P. 695,575, 1930; *Chem. Abs.*, 1931, 25, 2740. Cf. A. Klages and R. Keil, *Ber.*, 1903, 36, 1632.

<sup>235</sup> O. H. Smith and G. W. Jargstorff, U. S. P. 1,870,877, Aug. 9, 1932, to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, 26, 5580. Canadian P. 324,970, 1932, to Dominion Rubber Co., Ltd.; *Chem. Abs.*, 1932, 26, 5315. French P. 721,843, 1931; *Chem. Abs.*, 1932, 26, 4069.

<sup>236</sup> O. H. Smith, U. S. P. 1,926,314, Sept. 12, 1933, to Naugatuck Chemical Co.; *Chem. Abs.*, 1933, 27, 5757. See also O. H. Smith and G. W. Jargstorff, British P. 387,397, 1933; *Chem. Abs.*, 1933, 27, 4548. German P. 564,882, 1931; *Chem. Abs.*, 1933, 27, 1015.

highly concentrated styrene solution was obtained. Dorrough<sup>231</sup> formed the quaternary salt of pyridine and chloroethylbenzene and heated it at 375-400°C. Chloroethylbenzene may also be heated with inorganic catalysts, such as mercury salts or zinc chloride,<sup>237</sup> with strong acids, such as sulphuric or phosphoric,<sup>238</sup> or with weak organic acids.<sup>230</sup> Passage of  $\alpha$ -chloroethylbenzene over active carbon at atmospheric pressure and at 260°C. is another method.<sup>240</sup> Zal'kind, Berkovich and Amusin<sup>241</sup> chlorinated ethyl benzene at 70°C. in the presence of phosphorus pentachloride as a catalyst. This yielded styrene on boiling with quinoline, or by hydrolysis with dilute soda solution, followed by dehydration with dilute acid potassium sulphate solution. Bromoethylbenzene gives styrene by heating under ordinary pressure.<sup>242</sup>

Analogues of styrene may be obtained by heating the corresponding chloroethylbenzene derivatives with nitrogen-bases or their salts,<sup>243</sup> or with weak, difficultly volatile acids, such as boric, chloroacetic or palmitic.<sup>244</sup>

Deluchat<sup>245</sup> used quinoline for elimination of hydrogen bromide from *o*- or *m*-dibromodiethylbenzene to obtain *o*- and *m*-divinylbenzene.<sup>246</sup> *p*-Divinylbenzene may be prepared by a similar reaction.<sup>247</sup> A good yield of styrene is obtained by brominating ethylbenzene to styryl dibromide and treating the latter with magnesium.<sup>248</sup>

1,1-Dichloroethylbenzene, formed by the action of phosphorus pentachloride on acetophenone, breaks down on boiling in petroleum ether to give  $\alpha$ -chlorostyrene, a compound which resinifies easily.<sup>249</sup>

**Styrene from Hydrocarbons.** When ethylbenzene is passed through an iron tube heated at approximately 650°C., styrene is formed by elimination of hydrogen. The efficiency of the process may run as high as 32 per cent. Cracking of the various homologues of benzene such as xylene, yields styrene to the extent of about 6 per cent.<sup>250</sup> 1,3,5-Dimethylethylbenzene decomposes into 3,5-dimethylstyrene, whereas methylethylbenzene gives methylstyrene.<sup>251</sup> Berthelot<sup>252</sup> passed a mixture of ethylene and benzene through a red-hot tube and isolated styrene from the products of pyrolysis.

Instead of splitting off hydrogen, some hydrocarbons yield styrene by the elimination of methane or other hydrocarbon of low molecular weight. Cymene is said to give well over 50 per cent of *p*-methylstyrene.<sup>253</sup>

<sup>231</sup> G. L. Dorrough, U. S. P. 1,892,386, Dec. 27, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1897.

<sup>237</sup> G. W. Jargstorff, U. S. P. 1,870,852, Aug. 9, 1932, to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, 26, 5580.

<sup>238</sup> O. H. Smith, U. S. P. 1,870,878, Aug. 9, 1932; *Chem. Abs.*, 1932, 26, 5580.

<sup>239</sup> W. Krey, German P. 599,166, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5834. French P. 729,687, 1932; *Chem. Abs.*, 1933, 27, 313.

<sup>240</sup> E. Dorrer, German P. 559,737, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 737.

<sup>241</sup> Yu. S. Zal'kind, I. P. Berkovich and M. K. Amusin, *Plast. Mass.*, 1934, 1, 14; *Chem. Abs.*, 1934, 28, 5870.

<sup>242</sup> Thorpe, *Proc. Roy. Soc.*, 18, 123.

<sup>243</sup> British P. 396,079, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 905. French P. 729,730, 1932; *Chem. Abs.*, 1933, 27, 307.

<sup>244</sup> British P. 382,816, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 140. French P. 729,687, 1932; *Chem. Abs.*, 1933, 27, 313.

<sup>245</sup> R. Deluchat, *Compt. rend.*, 1931, 192, 1387; *Chem. Abs.*, 1931, 25, 4532.

<sup>246</sup> Quinoline or solid sodium hydroxide gives varnish-like polymers with diphenylcyclopropylmethyl chloride. P. Lipp, J. Buckkremer and H. Seeles, *Ann.*, 1932, 499, 1; *Chem. Abs.*, 1933, 27, 709.

<sup>247</sup> D. Lespieau and R. Deluchat, *Compt. rend.*, 1930, 190, 683; *Chem. Abs.*, 1930, 24, 2733. See also H. Ingle, *Ber.*, 1894, 27, 2528.

<sup>248</sup> J. v. Braun and K. Moldinke, *Ber.*, 1921, 54, 618.

<sup>249</sup> C. Dufraisse and J. E. Viel, *Bull. soc. chim.*, 1925, (4) 37, 874; *Chem. Abs.*, 1925, 19, 3263.

<sup>250</sup> I. Ostromislensky and M. G. Shepard, U. S. P. 1,541,175, June 9, 1925, to Naugatuck Chemical Co.; *Chem. Abs.*, 1926, 20, 424. Canadian P. 261,325, 1926; *Chem. Abs.*, 1926, 20, 3461. British P. 232,909, 1924; *Brit. Chem. Abs. B*, 1926, 299. German P. 476,270, 1924.

<sup>251</sup> I. Ostromislensky and M. G. Shepard, U. S. P. 1,552,874, Sept. 8, 1925; *Chem. Abs.*, 1925, 19, 3492.

<sup>252</sup> M. Berthelot, *Ann.*, 1867, 142, 257.

<sup>253</sup> I. Ostromislensky and M. G. Shepard, U. S. P. 1,552,875, Sept. 8, 1925; *Chem. Abs.*, 1925, 19, 3492.

Styrene is formed in the vapor-phase cracking of petroleum and at least some natural gases.<sup>254</sup> When petroleum is passed through a reaction tube with a stream of carbon dioxide or other inert gas at a temperature of 650°C., about 6 per cent of styrene is obtained.<sup>255</sup> One way of isolating styrene from the crude distillate, or from any other mixture, is to heat the solution for about 16 hours at 200°C. Polystyrene is formed and is recovered by steam distillation. It can be reconverted to styrene by heating at 350-500°C.<sup>256</sup> Styrene may be separated from a mixture with ethylbenzene by cooling the solution to a low temperature and filtering off the crystallized material.<sup>257</sup>

Vapor-phase cracking of aromatic hydrocarbons in the presence of dehydrogenation catalysts is a more efficient method. A mixture of ethylbenzene and steam may be led at 650°C. over silica gel, active carbon, or lime and magnesium oxide.<sup>258</sup> Styrene or vinyl naphthalene is produced when the vapor of ethylbenzene or ethyl naphthalene is passed at reduced pressure over cerium, copper, iron or zinc oxides heated at about 700°C.<sup>259</sup> The procedure can be improved by preliminary heating of the catalysts in nitrogen, hydrogen or steam.<sup>260</sup> Tungsten, molybdenum or uranium oxides act as promoters for other catalysts or they may be used alone. Various homologues of styrene are obtained when diethylbenzene, ethylbiphenyl, isopropylbenzene, ethyltoluene or the product of the reaction between propylene and benzene are decomposed.<sup>261</sup>

A mixture of benzene and ethylbenzene may be heated in the presence of hydrogen-acceptors, such as sulphur or a mixture of sulphur and ethylene dichloride, which favor dehydrogenation by combining with the hydrogen as fast as it is formed.<sup>262</sup> Ethylbenzene was also passed through a chromel tube at 675-725°C. in the presence of sulphur-free halogens or organic halides, such as ethylene chloride and carbon tetrachloride, to obtain styrene with a concentration of about 40 per cent.<sup>263</sup>

**Styrene by Dehydration of Alcohols.** Distillation of  $\beta$ -phenylethyl alcohol over anhydrous potassium hydroxide yields styrene almost quantitatively.<sup>264</sup> In like manner, distillation of p-diethylolbenzene gives p-divinylbenzene,<sup>265</sup> and  $\alpha$ -ethylolnaphthalene produces  $\alpha$ -vinyl naphthalene.<sup>266</sup> Dehydration with potassium

<sup>254</sup> S. F. Buch and E. N. Hague (*Ind. Eng. Chem.*, 1934, 26, 1008) discuss the formation of styrene and indene as pyrolysis products of Persian natural gases. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

<sup>255</sup> I. Ostromislenskij, U. S. P. 1,633,405, Sept. 4, 1928; *Chem. Abs.*, 1928, 22, 3893

<sup>256</sup> I. Ostromislenskij, U. S. P. 1,703,950, Mar. 5, 1929, *Chem. Abs.*, 1929, 23, 1911

<sup>257</sup> H. Mark and K. Wulff, German P. 534,476, 1930, to I. G. Farbenind. A.-G., *Chem. Abs.*, 1932, 26, 738

<sup>258</sup> H. Mark and K. Wulff, German P. 550,055, 1929; *Chem. Abs.*, 1932, 26, 4069. British P. 340,587, 1929; *Brit. Chem. Abs. B.*, 1931, 335. French P. 702,377, 1930; *Chem. Abs.*, 1931, 25, 4285.

<sup>259</sup> K. Wulff and E. Roell, U. S. P. 1,968,241, Jan. 1, 1935, to I. G. Farbenind. A.-G., *Chem. Abs.*, 1935, 29, 1101. German P. 563,395, 1930, *Chem. Abs.*, 1933, 27, 1015. British P. 371,537, 1930, *Brit. Chem. Abs. B.*, 1932, 793. French P. 721,597, 1931; *Chem. Abs.*, 1932, 26, 4061. See also French P. 40,673, 1931, addn. to 702,377; *Chem. Abs.*, 1933, 27, 1367, and French P. 762,672, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5081. Cf. H. Suida, U. S. P. 1,985,844, Dec. 25, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1099. Austrian P. 182,042, 1932, *Chem. Abs.*, 1933, 27, 2601.

<sup>260</sup> H. Mark and K. Wulff, German P. 560,686, 1930, addn. to 550,055, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1015.

<sup>261</sup> British P. 351,310, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 2990

<sup>262</sup> O. H. Smith, U. S. P. 1,870,876, Aug. 9, 1932, to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, 26, 5580. British P. 354,308, 1930; *Brit. Chem. Abs. B.*, 1932, 13. French P. 693,876, 1930; *Chem. Abs.*, 1931, 25, 1538. Canadian P. 308,122, 1931; *Chem. Abs.*, 1931, 25, 1266. German P. 800,268, 1924; *Chem. Abs.*, 1934, 28, 6448.

<sup>263</sup> W. A. Gibbons and O. H. Smith, U. S. P. 1,938,827, Dec. 12, 1933, to Naugatuck Chem. Co.; *Chem. Abs.*, 1934, 28, 1367.

<sup>264</sup> S. Sabatay, *Bull. soc. chim.*, 1929, 45, 69; *Chem. Abs.*, 1929, 23, 2427. I. Palfrey, S. Sabatay and D. Sontag, *Compt. rend.*, 1932, 195, 1392; *Chem. Abs.*, 1933, 27, 1624. Cf. S. Sabatay and T. Mintou, *ibid.*, 842; *Brit. Chem. Abs. A.*, 1930, 85.

<sup>265</sup> S. Sabatay, *Compt. rend.*, 1931, 192, 1109, *Chem. Abs.*, 1931, 25, 3973.

<sup>266</sup> I. Palfrey, S. Sabatay and D. Sontag, *Compt. rend.*, 1932, 194, 2065; *Chem. Abs.*, 1932, 26, 4325. According to D. Sontag (*Compt. rend.*, 1933, 197, 1130; *Chem. Abs.*, 1934, 28, 2349), distillation of  $\beta$ -ethylolnaphthalene leaves a resinous residue as a result of partial dehydration to  $\beta$ -vinyl naphthalene and polymerization of the latter. The  $\alpha$ -vinyl naphthalene form (D. Sontag, *Ang. chem.*,

hydroxide of a mixture of the o- and p-bromo derivatives of  $\beta$ -phenylethanol, obtained by bromination of the alcohol, gives o- and p-bromostyrene, which polymerize to light-colored resins.<sup>267</sup> Further experiments have shown<sup>268</sup> that the bromostyrene formed in this manner is very stable to heat and shows little tendency to polymerize. Substitution of chlorine for bromine in this treatment results in a chlorostyrene which is also little polymerized by heat. Nuclear substitution of halogens is effected by reacting in the cold in the presence of iron filings or iodine, the nuclear halogen atom not being affected by potassium hydroxide treatment. Formation of the mercaptans from the bromide compounds and subsequent potassium hydroxide treatment yielded styrene in the case of the  $\beta$ -phenylethylbromide, and also a small amount from the  $\alpha$ -isomer, contrary to the results experienced with the  $\alpha$ -alcohol. Von Braun and Neumann<sup>269</sup> obtained a polymer of o-divinylbenzene by treating the quaternary compound of methyl iodide and o-di-( $\beta$ -dimethylaminoethyl)-benzene with alkali. When  $\beta$ -phenylethyl phenylacetate is distilled styrene is formed.<sup>270</sup> Deluchat<sup>271</sup> produced o- and m-divinylbenzene respectively from o-di- $\alpha$ -bromopropylbenzene and m-di- $\alpha$ -bromoethylbenzene.

Distillation of  $\alpha$ -phenylethyl alcohol (phenylmethylcarbinol) over anhydrous potassium hydroxide does not give styrene, but the passage of this alcohol over alumina, thoria or tungsten oxide at 250-400°C. produces that compound in 90 per cent yield.<sup>272</sup> Phenylmethylcarbinol may also be dehydrated by heating it with phosphoric acid or by distilling its benzoic ester.<sup>273</sup>

Smith and Niederl<sup>274</sup> obtained o-vinylphenol by the reaction of phenol and ethylene oxide in the presence of concentrated sulphuric acid. It is assumed that hydroxyethyl phenyl ether is first formed and that this becomes dehydrated and undergoes rearrangement.

Styrene was procured from  $\alpha,\beta$ -dibromodiethyl ether and ethyl ether by means of the Grignard reaction, using magnesium phenyl bromide in ethereal solution. The ingredients were mixed and then refluxed 0.5 hour on the water bath.  $\beta,\beta$ -Ethoxyphenylethyl bromide was produced and converted into styrene by treatment with a zinc-copper couple.<sup>275</sup>

**Styrene by Decarboxylation of Acids.** Bonastre<sup>276</sup> isolated styrene in 1831 by distillation of liquid storax where it occurs in mixture with various cinnamic derivatives. Dragon's blood was also an early source of the compound.<sup>277</sup> When cinnamic acid is heated with barium hydroxide,<sup>278</sup> or when copper cinnamate<sup>279</sup> is heated, styrene is obtained. If cinnamic acid is treated with hydrogen bromide and the resulting bromo-acid boiled with soda solution, styrene is produced almost quantitatively by elimination of hydrogen bromide and carbon dioxide.<sup>280</sup> Careful distillation of cinnamic acid is a convenient method for its preparation.<sup>281</sup>

1934, 1, 359; *Chem. Abs.*, 1934, 28, 4716) is more apt to polymerize than the  $\beta$ -isomer, which is a solid with an intense odor of thymol.

<sup>267</sup> L. Palfray, S. Sabatay and D. Sontag, *Compt. rend.*, 1933, 196, 622; *Chem. Abs.*, 1933, 27, 3203

<sup>268</sup> D. Sontag, *Ann. chim.*, 1934, 1, 359; *Chem. Abs.*, 1934, 28, 4716.

<sup>269</sup> J. v. Braun and L. Neumann, *Ber.*, 1920, 53, 110

<sup>270</sup> H. Hibbert and C. P. Burt, *J. A.C.S.*, 1925, 47, 2240

<sup>271</sup> R. Deluchat, *Ann. chim.*, 1934, 1, 181; *Chem. Abs.*, 1934, 28, 3062

<sup>272</sup> E. Laage, German P. 533,827, 1925, to I. G. Farbenind. A.-G., British P. 338,262, 1929; *Brit. Chem. Abs.*, B, 1931, 238. French P. 682,569, 1929; *Chem. Abs.*, 1930, 24, 4523.

<sup>273</sup> A. Klages and P. Allendorff, *Ber.*, 1898, 31, 1003, 1298. The vinylphenylcarbinol and cinnamyl alcohol esters of  $\beta$ -anthraquinone-carboxylic acid have a tendency to form glassy melts, according to J. Meisenheimer, W. Schmidt and G. Schafer (*Ann.*, 1933, 501, 131, *Chem. Abs.*, 1933, 27, 2678)

<sup>274</sup> R. A. Smith and J. B. Niederl, *J.A.C.S.*, 1931, 53, 806.

<sup>275</sup> H. I. Waterman and W. J. C. de Kok, *Rec. trav. chim.*, 1934, 53, 1133; *Chem. Abs.*, 1935, 29, 1073.

<sup>276</sup> Bonastre, *J. de pharmacie*, 1831, 17, 338

<sup>277</sup> Glénard and Boudault, *Ann.*, 1845, 53, 325.

<sup>278</sup> Gerhardt and Cahours, *Ann.*, 1841, 38, 313.

<sup>279</sup> Hempel, *Ann.*, 1846, 59, 318.

<sup>280</sup> R. Fittig and F. Binder, *Ann.*, 1879, 195, 137. *J.C.S.*, 1876, 36, 378.

<sup>281</sup> I. Ostromislensky, U. S. P. 1,541,176, June 9, 1925, to Naugatuck Chemical Co; *Chem. Abs.*,

4-Hydroxy-3-methoxycinnamic acid when heated gives an oil (assumed to be 4-hydroxy-3-methoxystyrene) which resinifies easily.<sup>282</sup>

**Styrene from Acetylene.** Acetylene would seem to offer a source of styrene but no satisfactory process has been evolved as yet using this substance. Berthelot<sup>283</sup> found a small quantity of styrene among the pyrolytic products of acetylene. Also the reaction between acetylene and benzene in presence of aluminum chloride has been attempted. Varet and Vienne<sup>284</sup> reported an 80 per cent yield by this reaction but this has never been verified. On the contrary, Cook and Chambers<sup>285</sup> found only traces of styrene, and Böeseken and Adler<sup>286</sup> using a highly reactive preparation of aluminum chloride, obtained a product that was insoluble in all solvents and therefore was not polystyrene. It is known that aluminum chloride is a polymerization catalyst for styrene but the polymer thus formed is soluble. Böeseken and Adler<sup>286</sup> considered their product to be the polymer of a very reactive compound  $C_6H_5$  formed from acetylene and benzene, and called it *polyprotostyrene*. By introducing acetylene into a suspension of aluminum chloride in dry benzene what is described as a cuprene-like substance is obtained, an amorphous mass insoluble in all solvents.<sup>288</sup> Thus, the reaction of acetylene and benzene<sup>289</sup> does not yield styrene.<sup>290</sup> However, 2,4-dihydroxystyrene is the first product formed from acetylene and resorcinol in presence of a mercury catalyst. It forms an insoluble resin on standing.<sup>291</sup>

The Friedel-Crafts reaction of benzene and vinyl chloride yields neither styrene nor polystyrene.<sup>292</sup> Asym-diphenylethane, 9,10-dimethyldihydroanthracene and an anthracene-type resin are formed.

**Miscellaneous Sources of Styrene.**<sup>293</sup> Styrene was early recognized as a constituent of crude xylene.<sup>294</sup> Muller and Langedijk,<sup>295</sup> after prolonged boiling of a specimen of crude xylene, distilled it and obtained a residue of polystyrene equivalent to 17.9 per cent of the mixture. Styrene also occurs in distillates from brown-coal tar.<sup>296</sup>

1926, 20, 424 Canadian P. 261,326, 1926; T. W. Abbott and J. R. Johnson, *Org. Syntheses*, 1928, 8, 84. Cf. Howard, *Jahresber.*, 1860, 303; W. v. Miller, *Ann.*, 1877, 189, 339; G. Knaemer, A. Spilker and P. Eberhardt, *Ber.*, 1890, 23, 3269. For formation from cinnamic acid by fermentation, see Oliveira, *J. pharm. chim.* (6) 24, 62; *Chem. Zentr.*, 1906, 2, 608.

<sup>282</sup> K. Brand and G. Westerburg, *Arch. Pharm.*, 1931, 269, 326; *Brit. Chem. Abs. A.*, 1931, 953. See also T. Reichstein, *Helv. Chim. Acta*, 1932, 15, 1450; *Chem. Abs.*, 1933, 27, 1333.

<sup>283</sup> M. Berthelot, *Ann.*, 1867, 141, 181.

<sup>284</sup> R. Varet and G. Vienne, *Compt. rend.*, 1886, 64, 1375; *Chem. Zentr.*, 1887, 653. Cf. E. Parone, *L'Orosi*, 1902, 25, 148; *Chem. Zentr.*, 1903, 2, 662.

<sup>285</sup> O. W. Cook and V. J. Chambers, *J.A.C.S.*, 1921, 43, 334.

<sup>286</sup> J. Böeseken and A. A. Adler, *Rec. trav. chim.*, 1929, 48, 474; *Chem. Abs.*, 1929, 23, 2948.

<sup>287</sup> J. Böeseken and A. A. Adler, *loc. cit.*

<sup>288</sup> W. O. Herrmann, H. Deutsch and W. Haenel, U. S. P. 1,810,174, June 16, 1931, to Consort. f. elektrochem. Ind.; *Chem. Abs.*, 1931, 25, 4726. *British P.* 228,157, 1925; *J.S.C.I.*, 1925, 44, 771B.

<sup>289</sup> J. S. Reichert and J. A. Nieuwland (*J.A.C.S.*, 1923, 45, 3090) prepared unsym-diphenylethane by passing acetylene into benzene in the presence of concentrated sulphuric acid and a mercuric salt. Cf. J. A. Reilly and J. A. Nieuwland, *J.A.C.S.*, 1928, 50, 2564.

<sup>290</sup> p-Xylylene dibromide in toluene solution reacts with sodium by the Wurtz reaction to give an insoluble and infusible polymeric hydrocarbon of the same empirical formula,  $(C_8H_8)_n$ , as the product from acetylene and benzene. (See R. A. Jacobson, *J.A.C.S.*, 1932, 54, 1516.) In this case the structure of the polymer is assumed to be a long chain of p-xylylene groups,  $(-CH_2C_6H_4CH_2-)_n$ . Another insoluble polymer of the same empirical formula is noted in the product obtained by treating phenylethyl chloride with aluminum chloride, which may be represented by the formula,  $(-C_6H_4C_2H_4-)_n$ . (See J. v. Braun and H. Deutsch, *Ber.*, 1912, 45, 1268.) The reaction product of benzene and acetylene may be of the same type and consist of chains of the group:  $(-C_6H_4-C_2H_4-)_n$ . These several products differ from polystyrene in having benzene rings as links of the chain molecule.

<sup>291</sup> S. A. Flood and J. A. Nieuwland, *J.A.C.S.*, 1928, 50, 2566. Cf. R. H. Wenzke and J. A. Nieuwland, *ibid.*, 1924, 46, 179.

<sup>292</sup> J. M. Davidson and A. Lowy, *J.A.C.S.*, 1929, 51, 2978. Cf. J. Böeseken and M. C. Bastet, *Rec. trav. chim.*, 1913, 32, 184; *Chem. Abs.*, 1914, 8, 1270.

<sup>293</sup> For additional information on the formation of styrene and polystyrene see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., N. Y., 1934.

<sup>294</sup> M. Berthelot, *Ann. Suppl.*, 1865, 3, 368.

<sup>295</sup> H. D. Muller and S. L. Langedijk, *Chem. Weekblad*, 1923, 20, 627; *J.S.C.I.*, 1924, 43, 9 B.

<sup>296</sup> G. Schultz and K. Würth, *J. Gasbel.*, 1905, 48, 125, 152, 177, 200; *Chem. Zentr.*, 1905, 1, 1444.



A considerable amount of styrene is found in carburetted water gas<sup>297</sup> and it is present in the light oil obtained in the manufacture of water gas to the extent of 1.5 to 2 per cent.<sup>298</sup>

In the presence of oxygen in the gas, styrene and similar constituents, such as indene and cyclopentadiene, polymerize to form resins which deposit in gas mains and on the leather diaphragms of gas meters. Such substances are admittedly industrial nuisances and gas manufacturers welcome all efforts to remove these gum-forming materials. It has been estimated that there is a potential supply in the United States of 8,000,000 pounds per year of styrene in the drip-oil of carburetted water gas.<sup>299</sup> Brown<sup>300</sup> suggested its recovery from this source by fractionation of the oil. However, the cost of collection would appear to be prohibitive.

The resinous material formed by polymerization and oxidation of the unsaturated compounds in manufactured gas is called *liquid-phase gum* and occurs mainly in carburetted water gas and mixed gases.<sup>301</sup> Another type known as *vapor-phase gum* results from reaction of gum-forming compounds with oxides of nitrogen.<sup>302</sup> The latter type is formed in the gas phase and is finely dispersed in the gas. It occurs mainly in coal and coke-oven gases.<sup>303</sup> The gum particles are for the most part highly charged and tend to coalesce, finally dropping out of suspension.<sup>304</sup>

The addition of phenols to gases has been suggested as a means of preventing gum deposits in gas mains.<sup>305</sup> Phenols are generally negative oxidation and polymerization catalysts. The removal of oxides of nitrogen also aids in preventing gum formation in gas.<sup>306</sup>

#### POLYMERIZATION OF STYRENE DERIVATIVES

Substitution in the benzene nucleus of styrene gives compounds having the same polymerizing tendency as styrene itself, and it may be even more pronounced. On the other hand, substitution in the ethylene side chain greatly lessens this tendency, depending somewhat upon the kind of group that is introduced. Resin-forming ability should be judged not only by the ease in which polymers form but also by the size of the molecules thus produced. In cases where molecular weight data are lacking, the physical properties of the polymer indicate the degree of polymerization. High polymers are tough; low polymers are brittle. Also soluble polymers of high molecular weight are precipitated from their solutions, when a non-solvent is added, in the form of soft flocks or fibers. Compounds of low molecular weight come down as finely crystalline or amorphous powders.

The effect of a methyl group may be illustrated by comparing styrene compounds containing this group in the ring and in the side chain. o-Methylstyrene polymerizes more readily than the unsubstituted compound, and p-methylstyrene rapidly forms a tough, elastic, resinous material when heated.<sup>307</sup> Also m-methyl-

<sup>297</sup> R. S. Andrews, *Gas J.*, 1931, 193, 158, 212; *Chem. Abs.*, 1931, 25, 2268.

<sup>298</sup> N. A. Orlov, *Zhur. Prikladnoi Khim.*, 1930, 3, 585; *Chem. Abs.*, 1931, 25, 1972.

<sup>299</sup> R. L. Brown, *Ind. Eng. Chem.*, 1928, 20, 1178.

<sup>300</sup> R. L. Brown, U. S. P. 1,640,975, Aug. 30, 1927; *Chem. Abs.*, 1927, 21, 3449.

<sup>301</sup> A. L. Ward, C. W. Jordan and W. H. Fulweiler, *Ind. Eng. Chem.*, 1932, 24, 969; 1933, 25, 1224.

According to A. Engelhardt and H. Rüping (*Gas- u. Wasserfach*, 1933, 76, 478; *Brit. Chem. Abs. B*, 1933, 611), the active charcoal method of removing benzol from illuminating gas is more efficient than the wash-oil method, and also removes more of the gum-forming constituents from gas. For further information regarding treatment of styrene-containing gases, see W. W. Odell, U. S. P. 1,925,151, Sept. 5, 1933 and 1,926,048, Sept. 12, 1933; *Chem. Abs.*, 1933, 27, 5520, 5944. Also D. L. Jacobson and W. L. Shively, U. S. P. 1,932,525, Oct. 31, 1933, to Koppers Co.; *Brit. Chem. Abs. B*, 1934, 822. W. L. Shively, U. S. P. 1,945,001, Jan. 30, 1934, to Koppers Co.; *Chem. Abs.*, 1934, 28, 2510.

<sup>302</sup> G. Berkhoff, *Het Gas*, 1931, 51, 460; *Chem. Abs.*, 1932, 26, 1755.

<sup>303</sup> W. H. Fulweiler, *Gas J.*, 1932, 200, 570; *Brit. Chem. Abs. B*, 1933, 49. See also Chapter 35.

<sup>304</sup> C. W. Jordan, A. L. Ward and W. H. Fulweiler, *Ind. Eng. Chem.*, 1934, 26, 947, 1028.

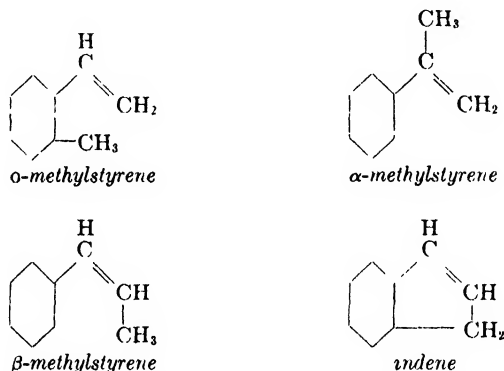
<sup>305</sup> W. H. Fulweiler, *British P.* 336,456, 1928, to Humphrey & Glasgow, Ltd.; *Chem. Abs.*, 1931, 25,

1976.

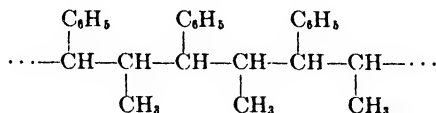
<sup>306</sup> K. Bunte, *Gas und Wasserfach*, 1934, 77, 81; *Chem. Abs.*, 1934, 28, 2877.

<sup>307</sup> I. Ostromislensky, U. S. P. 1,683,402, Sept. 4, 1928; *Chem. Abs.*, 1928, 22, 3893. *British P.* 236,891, 1925; *J.S.C.I.*, 1925, 44, 771B.

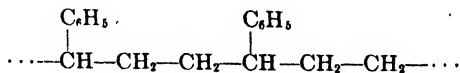
styrene solidifies when allowed to stand or when heated.<sup>308</sup> These compounds stand in contrast with  $\alpha$ -methylstyrene (isopropenylbenzene) which does not polymerize at ordinary temperature either on long standing or by the action of light. When stannic chloride is added a violent reaction occurs but the degree of polymerization is not high, a mixture of polymers ranging from the dimer to the octamer being produced.<sup>309</sup> The effect of a methyl group on the  $\beta$ -carbon is noted from the behavior of  $\beta$ -methylstyrene (propenylbenzene), which is converted to a low polymer (apparently the dimer) when boiled with metallic sodium.<sup>310</sup> Indene has a structure which would suggest a  $\beta$ -substituted styrene. However, the ease with which it polymerizes shows that it is more nearly related to *o*-methylstyrene, although it does not form extremely high polymers. (See Chapter 5.)



When heated alone propenylbenzene does not polymerize. Also it does not polymerize when heated with catalysts like stannic chloride. However, in the presence of boron fluoride a clear, brittle resin is formed. *p*-Methoxy- and *p*-ethoxy-propenylbenzene polymerize more easily and mild catalysts are effective. In no case does the reaction go as rapidly as with styrene, nor can eucolloids be obtained. The structure of polypropenylbenzene has been assumed to be:



However, viscosity determinations indicate a chain length 50 per cent greater than is apparent from cryoscopic determination of molecular weight. Therefore, instead of a 1,2 addition as was formerly supposed it is suggested that 1,3 addition occurs:

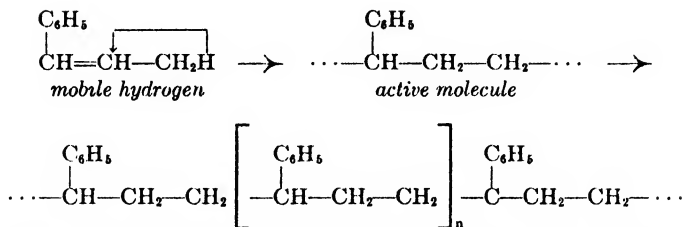


The mechanism of this reaction involves the wandering of a terminal hydrogen atom in the side chain:

<sup>308</sup> W. Müller, *Ber.*, 1887, 20, 1216

<sup>309</sup> H. Staudinger and F. Breusch, *Ber.*, 1929, 62, 442; *Chem. Abs.*, 1929, 23, 3213. See also E. Bergmann, H. Taubadel and H. Weiss, *Ber.*, 1931, 64, 1493; *Chem. Abs.*, 1931, 25, 4239.

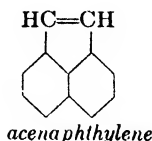
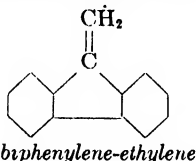
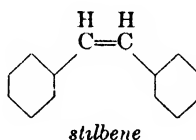
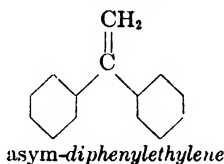
<sup>310</sup> G. Errera, *Gazz. chim. ital.*, 1885, 14, 509; *J.C.S.*, 1885, 48, 772.



Proof that the polymerization reaction is different than with styrene is indicated by the products obtained by cracking polypropenylbenzene. Besides the monomer, a small amount of 1,4-diphenylbutadiene is present.<sup>310a</sup>

Many styrene derivatives have been studied which contain groups in the benzene nucleus. In most cases polymers of high molecular weight are formed. p-Ethylstyrene<sup>311</sup> when heated to its boiling point changes slowly to a viscous liquid which solidifies on cooling. 2,4-Dimethylstyrene<sup>312</sup> produces a tough, elastic polymer which is insoluble. p-Isopropylstyrene polymerizes more easily than styrene itself.<sup>313</sup> 2,4,5-Trimethylstyrene shows considerable thickening when heated at its boiling point,<sup>314</sup> but sym-trimethylstyrene polymerizes more slowly, although it forms a resin when treated with concentrated sulphuric acid.<sup>315</sup> p-Chlorostyrene<sup>316</sup> and o-bromoethylstyrene<sup>317</sup> change readily to solid forms on standing. p-Nitrostyrene when heated gives a polymer which is insoluble in all solvents.<sup>318</sup>  $\beta$ -Nitrostyrene forms an amorphous solid when treated with alkaline materials such as sodium malonic ester<sup>319</sup> or ammonia, hydrazine and sodium methylate.<sup>320</sup>

Phenyl groups on the side chain greatly limit the size of the polymer. In the absence of oxygen, asym-diphenylethylene forms no polymer higher than the dimer.<sup>321</sup> However, there are two possible dimers, one unsaturated and the other saturated. The first is 1,1,3,3-tetraphenyl-1-butene and the second is 1,1,3-triphenyl-3-methylhydriene.<sup>322</sup> Oxidation of asym-diphenylethylene leads to an insoluble polymeric product.<sup>323</sup> Diphenylene-ethylene is rapidly converted by heat or light



<sup>310a</sup> H. Staudinger and E. Dreher, *Ann.*, 1935, 517, 73.

<sup>311</sup> A. Klages and R. Keil, *Ber.*, 1903, 36, 1633.

<sup>312</sup> I. Ostromislensky, *loc. cit.* See also A. Klages, *Ber.*, 1902, 35, 2249.

<sup>313</sup> W. H. Perkin, *J.C.S.*, 1877, 32, 663.

<sup>314</sup> A. Klages and R. Keil, *Ber.*, 1903, 36, 1641.

<sup>315</sup> A. Klages and P. Allendorff, *Ber.*, 1898, 31, 1010.

<sup>316</sup> H. Staudinger and E. Suter, *Ber.*, 1920, 53, 1092.

<sup>317</sup> J. v. Braun, *Ber.*, 1917, 50, 45; *Chem. Abs.*, 1917, 11, 2785.

<sup>318</sup> A. Basler, *Ber.*, 1883, 16, 2006.

<sup>319</sup> P. Herrmann and D. Vorländer, *Abhandl. Natur. Ges. Halle*, 1899, 21, 251. *Chem. Zentr.*, 1899, 1, 730.

<sup>320</sup> D. E. Worrall, *J.A.C.S.*, 1927, 49, 1598, 1605.

<sup>321</sup> S. V. Lebedev, I. Andreevski and A. Matiuskina, *Ber.*, 1923, 56, 2349; *Chem. Abs.*, 1924, 18, 1123.

<sup>322</sup> E. Bergmann and H. Weiss, *Ann.*, 1930, 480, 49; *Chem. Abs.*, 1930, 24, 3503. C. S. Schoepfle and J. D. Ryan, *J.A.C.S.*, 1930, 52, 4021.

<sup>323</sup> H. Staudinger, *Ber.*, 1925, 58, 1075; *Chem. Abs.*, 1925, 19, 2658.

to an amorphous powder, possibly tribiphenylene-cyclohexane.<sup>324</sup> Acenaphthylene yields polyacenaphthylene,  $(C_{12}H_8)_{22}$ , on being heated above its melting point.<sup>325</sup> This is soluble in benzene and is precipitated as a colorless, amorphous powder when alcohol is added. In a benzene solution stilbene forms a dimer under the influence of light.<sup>326</sup> On exposure to light and air, resinous products are obtained besides benzoic acid.<sup>327</sup> In the presence of maleic anhydride, stilbene yields a heteropolymer<sup>328</sup> of a high molecular weight, but by itself it has rather mild polymerizing tendencies. These phenylated derivatives,<sup>329</sup> which form relatively low polymers, may be contrasted with the analogous  $\alpha$ -naphthylethylene ( $\alpha$ -vinyl-naphthalene)<sup>330</sup> which forms well-defined resins.

#### PHENOLIC STYRENES

o-Hydroxystyrene<sup>331</sup> on standing resinifies to a glass-like mass, insoluble in alkalis. When treated with concentrated sulphuric acid a dark red resin is formed. It is doubtful whether the degree of polymerization in this resin is very high since the phenolic group would be expected to act as a negative catalyst. o-Hydroxystyrene may be compared with cumarone which resinifies easily. (See Chapter 5.)

When o-methoxystyrene is heated at 150°C. it polymerizes and, when cold, is a transparent mass.<sup>332</sup> p-Methoxystyrene forms highly polymerized resins. When the reaction occurs at low temperatures the resin molecule may contain as high as a thousand monomeric groups.<sup>333</sup> Of the three methoxystyrenes, the meta- compound polymerizes most readily, then the ortho-, and finally the para-compound.<sup>334</sup> Vinyl derivatives of phenols or cresols are made by reacting vinyl halides with the aromatic compounds in the presence of aluminum chloride or other metallic halides. These may then be polymerized by heat or ultraviolet light.<sup>335</sup>

Eugenol, safrole and methylchavicol undergo very little polymerization. However, when heated with alcoholic potash their allyl groups are rearranged to propenyl groups, giving the so-called iso-compounds,<sup>336</sup> isoeugenol, isosafrole and anethole, respectively. These are methyl-substituted styrenes and as such they show mild polymerizing tendencies, at least much greater than the parent substances. Grognot<sup>337</sup> resinified eugenol in oil of cloves by treatment with phosphorus pentoxide. A brittle product resembling colophony resulted, with indications that some oxidation had occurred.

<sup>324</sup> H. Wieland, F. Reindel and J. Ferrer, *Ber.*, 1922, 55, 3313; *Chem. Abs.*, 1923, 17, 754; J. Ferrer, *Anal. soc. espan. fis. quim.*, 1922, 50, 459; *Chem. Abs.*, 1923, 17, 3177.  
<sup>325</sup> K. Dziewonski and T. Stolyho, *Ber.*, 1924, 57, 1531. See also K. Dziewonki and Z. Leyko, *Ber.*, 1914, 47, 1635.

<sup>326</sup> G. Ciamician and P. Silber, *Ber.*, 1903, 36, 4266.

<sup>327</sup> G. Ciamician and P. Silber, *ibid.*, 4129.

<sup>328</sup> T. Wagner-Jauregg, *Ber.*, 1930, 63, 3213; *Chem. Abs.*, 1931, 25, 2418. See also R. Kulin and T. Wagner-Jauregg, *Ber.*, 1930, 63, 2662; *Brit. Chem. Abs. B.*, 1930, 1580.

<sup>329</sup> Thermal decomposition of phenyl fumarate affords stilbene. However, if substituents are present in the phenyl group the products are frequently resins. R. Anschütz, *Ber.*, 1927, 60, 1320.

<sup>330</sup> L. Palfray, S. Sabatay and D. Sontag, *Compt. rend.*, 1932, 194, 2065; *Chem. Abs.*, 1932, 26, 4325. See also W. E. Lawson, U. S. P. 1,982,676, Dec. 4, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 526. British P. 355,032, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B.*, 1931, 1064.

<sup>331</sup> K. Fries and G. Fickewirth, *Ber.*, 1908, 41, 367. See also R. A. Smith and J. B. Niederl, *J.A.C.S.*, 1931, 53, 806.

<sup>332</sup> W. H. Perkin, *Ber.*, 1878, 11, 515.

<sup>333</sup> H. Stobbe and K. Toepfer, *Ber.*, 1924, 57, 484.

<sup>334</sup> A. Klages, *Ber.*, 1903, 36, 3588.

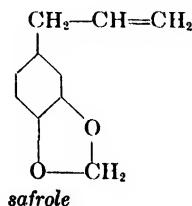
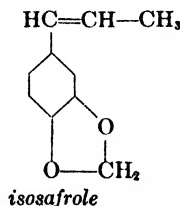
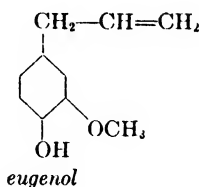
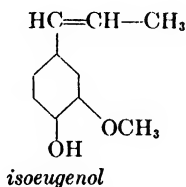
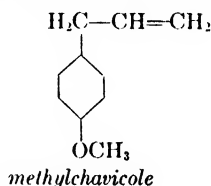
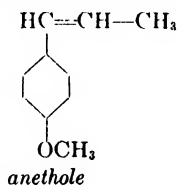
<sup>335</sup> British P. 409,132, 1932, to British Celanese, Ltd.; *Brit. Chem. Abs. B.*, 1934, 534.

<sup>336</sup> R. Priester, *Reichstoffsind.*, 1930, 5, 83, 108; *Brit. Chem. Abs. A.*, 1931, 470.

<sup>337</sup> L. Grognot, *Rev. gen. chim.*, 1907, 10, 49, *Chem. Abs.*, 1907, 1, 1179.

Polyanethole can be prepared from anethole in various ways. It occurs only in a hemicolloidal form. Treatment of anethole with stannic chloride yields the polymer as a white amorphous powder containing about 30 monomeric groups per molecule.<sup>338</sup> This is in contrast with p-methoxystyrene, noted above, whose molecule lacks substitution on the  $\beta$ -carbon of styrene and which therefore can yield eucoloidal forms. A colorless resin has been obtained as a residue in distilling p-propenylphenol.<sup>339</sup>

Ciamician and Silber<sup>340</sup> compared the action of safrole and isosafrole when exposed to sunlight. To both, traces of iodine were added and after protracted exposure the safrole was found to distil almost completely with steam, leaving only a trace of resinous material, while isosafrole was converted into a brittle brown resin. From 38 g. of isosafrole, 34 g. of resin were obtained. Methyleugenol similarly treated was unchanged but isomethyleugenol yielded a yellowish-brown, almost solid mass. Thirty-five g. of the iso-compound produced about 33 g. of resin, which dissolved completely in ether and made a sort of varnish. Whitby and Katz<sup>341</sup> used stannic chloride as a polymerization catalyst for isosafrole and isoeugenol. They found the molecular weights of the polymers prepared at ordinary temperatures to be about 2000. Prepared at about 200°C., the polymers showed half this molecular weight. The polymers are unsaturated. Eugenol and safrole give the same type of resins as the iso-compounds but the reaction goes much more slowly. Kronstein<sup>342</sup> heated safrole, eugenol, isosafrole and isoeugenol,



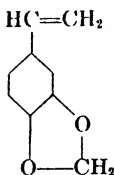
<sup>338</sup> H. Staudinger and M. Brunner, *Helv. Chim. Acta*, 1929, 12, 972; *Chem. Abs.*, 1930, 24, 613.

<sup>339</sup> A. Quilico and M. Freri, *Gazz. chim. ital.*, 1929, 59, 600; *Chem. Abs.*, 1930, 24, 599. Introduction of salt-forming groups into polymerized propenylphenols yields substances which arrest blood-coagulation. British P. 355,574, 1930, to F. Hoffmann-LaRoche & Co., A.-G.; *Brit. Chem. Abs. B.*, 1932, 80. W. H. Moss (Canadian P. 318,932, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 2072) made a resin for use in films and lacquers by condensing allyl alcohol with o-cresol in the presence of fused zinc chloride.

<sup>340</sup> G. Ciamician and P. Silber, *Ber.*, 1909, 42, 1389.

<sup>341</sup> G. S. Whitby and M. Katz, *Can. J. Research*, 1931, 4, 487; *Chem. Abs.*, 1931, 25, 4246.

<sup>342</sup> A. Kronstein, U. S. P. 843,401, Feb. 5, 1907; *Chem. Abs.*, 1907, 1, 918. British P. 17,378, 1900; *J.S.C.I.*, 1901, 20, 1123.



vinyl-3,4-pyrocatechol methylene ether

in the absence of oxygen, to temperatures below their decomposition points. He obtained polymerized substances, soluble in alcohol and ether, resembling natural soft resins. Heavy camphor oil undergoes a similar change. When safrole is passed at 500°C. over kieselguhr, it yields resinous products.<sup>343</sup>

Vanillin is obtained by hydrolysis of the ozonide of isoeugenol. Manufacturers of synthetic vanillin seek to avoid the formation of resin during the ozonation and hydrolysis of the ozonide. Resin formation is lessened by conducting the ozonolysis at a low temperature.<sup>344</sup> Methylation of the phenolic group is also effective.<sup>345</sup> Treatment of isoeugenol dissolved in toluene results in less resinous material than when the reaction is conducted in aqueous emulsion.<sup>346</sup> Harries<sup>347</sup> was able to limit resinification by treating the ozonide with potassium ferrocyanide in acetic acid solution. The ozonides of safrole and isosafrole decompose spontaneously at ordinary temperatures with formation of resins.<sup>348</sup>

Electrolytic oxidation of isoeugenol and vanillin in a 15 per cent solution of caustic soda yields resinous masses.<sup>349</sup> Resins are also formed by oxidation of isoeugenol in sodium sulphate solution with an anode of lead peroxide, unless the phenol group is protected by methylation.<sup>350</sup>

<sup>343</sup> Ramart-Lucas and P. Amagat, *Bull. soc. chim.*, 1932, (4) 51, 108; *Brit. Chem. Abs.* A, 1932, 505.

<sup>344</sup> E. Briner, R. Patry and E. deLussena, *Helv. Chim. Acta*, 1924, 7, 62; *Chem. Abs.*, 1924, 18, 1824.

<sup>345</sup> E. Briner, H. v. Tschärner and H. Paillard, *Helv. Chim. Acta*, 1925, 8, 406; *Chem. Abs.*, 1926, 20, 181.

<sup>346</sup> French P. 421,784. See *J.S.C.I.*, 1922, 41, 70R.

<sup>347</sup> C. Harries, German P. 321,567, 1918; *J.S.C.I.*, 1917, 36, 359.

<sup>348</sup> S. Nagai, *J. Chem. Ind. (Japan)*, 1922, 25, 1409; *Chem. Abs.*, 1923, 17, 2110; *J. Fac. Eng. Tokyo*, 1923, 13, 185; *J.S.C.I.*, 1924, 43, 838B.

<sup>349</sup> A. Lowy and C. M. Moore, *Trans. Am. Electrochem. Soc.*, 1922, 42, 273; *Chem. Abs.*, 1922, 16, 3815.

<sup>350</sup> F. Fichter and A. Christen, *Helv. Chim. Acta*, 1925, 8, 332; *Chem. Abs.*, 1925, 19, 2195.

## Chapter 12

# Miscellaneous Resins From Hydrocarbons and From Phenols. Certain Tars

### HYDROCARBON-ALDEHYDE RESINS

The interaction of aromatic hydrocarbons with aldehydes has been known at least since 1872 when Baeyer<sup>1</sup> condensed benzene and formaldehyde. Similar work was done by others at this time. Substances used included benzene, toluene, mesitylene, diphenyl, naphthalene, formaldehyde, acetaldehyde, methylal, and chloral.<sup>2</sup> The compounds obtained were generally of the diarylmethane type, and little or no account was taken of resin-forming tendencies in these condensations.

Nastyukov<sup>3</sup> condensed formaldehyde and benzene in the presence of sulphuric acid and obtained an insoluble amorphous solid which he found to be very stable to oxidizing agents. Repeating the experiment with naphthalene he decided that this type of condensation product was characteristic of unsaturated cyclic hydrocarbons and the percentage weight isolated was denoted as the "Formolite Number" of an oil so treated.<sup>4</sup> The same method was used by Arnold<sup>5</sup> in his investigation of low-temperature tar oils.

However, it was about 1907 that aromatic hydrocarbons, particularly naphthalene, became prominent as useful starting materials for resin production by virtue of their condensation with formaldehyde. It was reported that the products were soluble in oils, in hydrocarbons, in their chloro derivatives, and in some cases even in drying oils. Bohn<sup>6</sup> devised several procedures for making such resins. The following is an example of one of them:

To a solution of 8 parts of 30 per cent formalin, or its equivalent of methylal, in 115 parts of 97 per cent sulphuric acid is added 10 parts of naphthalene. The reaction is carried out for about 1½ hours at 110°C., in which time the mixture thickens. Treatment of the cooled product with water removes the catalyst and with benzene and alcohol removes any unchanged hydrocarbon. A bright yellowish-brown resin is finally obtained.

Bohn stated that the use of one molecular proportion (or greater) of formaldehyde yielded resins of higher melting point than those obtained with smaller

<sup>1</sup> A. Baeyer, *Ber.*, 1872, 5, 1094; *J.C.S.*, 1873, 26, 501.

<sup>2</sup> A. Baeyer, *Ber.*, 1873, 6, 220; *J.C.S.*, 1873, 26, 884. *Ber.*, 1874, 7, 1190; *J.C.S.*, 1875, 28, 148. J. Weiler, *Ber.*, 1874, 7, 1181; *J.C.S.*, 1875, 28, 151. O. Fischer, *Ber.*, 1874, 7, 1191; *J.C.S.*, 1875, 28, 154. J. Grabowski, *Ber.*, 1874, 7, 1605; *J.C.S.*, 1875, 28, 455.

<sup>3</sup> A. M. Nastyukov, *J. Russ. Phys.-Chem. Soc.*, 1903, 35, 824; 1904, 36, 881; *J.C.S.*, 1904, 86 (1), 242, 801.

<sup>4</sup> See also A. M. Nastyukov and K. L. Malyarov, *J. Russ. Phys.-Chem. Soc.*, 1910, 42, 1596; *J.C.S.*, 1911, 100 (1), 249. A. M. Nastyukov and N. V. Gurin, *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 46; *J.C.S.*, 1915, 108 (1), 227. A. M. Nastyukov, British Patent 289,920, 1927; *Chem. Abs.*, 1929, 23, 968; *J. Chem. Ind. (Russia)*, 1925, 1 (4), 28; *Brit. Chem. Abs. B*, 1926, 860. B. T. Brooks, "The Chemistry of the Non-benzenoid Hydrocarbons," The Chemical Catalog Co., 1922, 286.

<sup>5</sup> H. Arnold, *Z. angew. Chem.*, 1923, 36, 545; *Chem. Abs.*, 1924, 18, 1190.

<sup>6</sup> R. Bohn, U. S. P. 898,307, Sept. 8, 1908, to Badische Anilin- & Soda-Fabrik; *Chem. Abs.*, 1909, 3, 883.

proportions.<sup>7</sup> It was suggested that the products could be used in making varnishes and sealing wax.<sup>8</sup>

Hydrocarbons were condensed with formaldehyde (40 per cent) in the presence of concentrated sulphuric acid (sp. gr. 1.84) in a process employed by Bayer & Co.<sup>9</sup> The acid formed less than 60 per cent of the mixture. At 110-115°C. naphthalene yielded a white resin, soluble in acetone, benzene, solvent naphtha, carbon tetrachloride and carbon disulphide. Phenanthrene gave a brownish-yellow, brittle resin, soluble in benzene and xylene; and anthracene, a yellow resin soluble in benzene. Under pressure at 118-125°C., benzene formed a soft brown resinous mass soluble in benzene; toluene, a clear liquid, soluble in ether, acetone, benzene, and carbon tetrachloride; and xylene, a brown resin soluble in acetone, benzene, carbon tetrachloride and solvent naphtha. These products, especially those melting below 100°C., were thought to be of value in varnish making.

Condensation products of naphthalene with formaldehyde, intended for use in the lacquer or varnish industry, were prepared by Folchi<sup>10</sup> as follows:

One hundred grams of naphthalene are added to 80 cc. of 30 per cent formaldehyde, 100 cc. of sulphuric acid (sp. gr. 1.84) gradually added, and the mixture heated under reflux on a water bath at 80°C. for 1½ hours with agitation. The contents of the flask are poured into water at 80-90°C. and the melted condensation product is washed with water, dilute alkali, and with water again. The mass is then dried at 80°C. for 4 to 5 hours. For use as lacquer the material is melted with a small quantity of turpentine and mixed with refined tar. By strict attention to the above reaction conditions a weight yield of 100-110 per cent of the naphthalene used may be obtained. The hardness of the product varies with the temperature of formation. An alternative method is to use 100 grams of naphthalene, 80 grams of 40 per cent formaldehyde, and 120 grams of sulphuric acid, heating for 3 hours at 90-95°C. In this case the yield is 80-90 per cent. Folchi stated that the action of formaldehyde on unsaturated aliphatic hydrocarbons gave rubbery masses and the action on aromatic hydrocarbons gave materials similar to phenol-aldehyde resins.

La Vingtrie<sup>11</sup> mixed a naphthalene-formaldehyde resin with rubber, and by vulcanizing with sulphur obtained an ebonite. The resin was prepared as follows: 1 part of naphthalene is dissolved in 2 parts of concentrated sulphuric acid and heated with 3 parts of 13 per cent formalin at 140°C. in an autoclave. The product is purified by washing with water and caustic soda solution. Depending on conditions, the resin may have a melting point of 100°C. and be soluble in such solvents as carbon tetrachloride, or it may be an insoluble powder. A similar reaction was carried out by Aimond.<sup>12</sup> Naphthalene was converted into its sulphonic acid, using concentrated sulphuric acid, and then condensed with formaldehyde at 140°C. to yield a resin (Naphthoform A) which was infusible and insoluble. When introduced into ebonite it speeded the vulcanization. It was discovered that if the naphthalene was first treated with formaldehyde, and then mixed with sulphuric acid, the resulting resin (Naphthoform B) was fusible, melting at 100-120°C.

The last-noted examples have all used sulphuric acid as catalyst, but other catalysts have been found effective in some cases. For instance, aromatic hydrocarbons, or derivatives, are heated with aldehydes, preferably in a solvent such as acetic acid, with the use of such limited proportions of phosphoric or halogen

<sup>7</sup> R. Bohn, German P. 207,743, 1907, to Badische Anilin- & Soda-Fabrik; *J.S.C.I.*, 1909, 28, 431. British P. 16,245, 1907. French P. 386,664, 1908; *J.S.C.I.*, 1908, 27, 457, 695.

<sup>8</sup> The use of this resin in linoleum was suggested by F. Fritz, *Chem. Ztg.*, 1933, 57, 997; *Chem. Abs.*, 1934, 28, 2925.

<sup>9</sup> German P. 349,741, 1918, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1922, 41, 640A.

<sup>10</sup> P. Folchi, *Chem. Ztg.*, 1922, 46, 714; *J.S.C.I.*, 1922, 41, 720A.

<sup>11</sup> C. M. Bayard de la Vingtrie, French P. 493,569, 1920, and addition 22,728, 1920; *Kunststoffe*, 1922, 12, 172. For a comparison of the products obtained by Bohn, Folchi, and la Vingtrie, see A. Hutin, *Rev. prod. chim.*, 1922, 25, 797; *Chem. Abs.*, 1923, 17, 641. See also J. H. Frydlander, *Kunststoffe*, 1922, 12, 172; *Rev. prod. chim.*, 1922, 25, 653; *Chem. Abs.*, 1923, 17, 1156.

<sup>12</sup> L. Aimond, *Caoutchouc et Gutta-percha*, 1933, 30, 1652; *Brit. Chem. Abs.* B, 1933, 855.



acids that products soluble in linseed oil are obtained.<sup>13</sup> By using as condensing agents organic acids such as formic, oxalic or lactic, and varying the amount of formaldehyde used, the products will range from viscous oils to brittle resins. Other condensing agents include sodium bisulphate, stannous chloride, zinc chloride,<sup>14</sup> calcium chloride and magnesium sulphate.<sup>15</sup> Hydrocarbon derivatives which have been used are phenetole, anisole, diphenyl ether, m-cresol ethyl ether,  $\alpha$ -naphthyl ethyl ether and  $\beta$ -naphthyl ethyl ether.

Experiments performed in the author's laboratory<sup>16</sup> have demonstrated that resinous products are obtained when benzene and formaldehyde are condensed with zinc chloride and hydrogen chloride. Dry hydrogen chloride was passed for 25 minutes at 65°C. through a well-stirred mixture of benzene (200g.), 40 per cent formalin (35g.) and zinc chloride (50g.). The reaction product was subjected to steam-distillation to remove liquid components, leaving as a residue a dark violet, nearly black resin (yield 40%), insoluble in alcohol and acetone.

Benzaldehyde has been used in place of formaldehyde for condensation when the cyclic hydrocarbon contains eight or more carbon atoms.<sup>17</sup> Condensing technical xylene, or solvent naphtha, with benzaldehyde in the presence of concentrated sulphuric acid at less than 20°C. for 24 hours yields an oily product. This oil is steam-distilled to remove unaltered hydrocarbons, and the wax-like still-residue is purified by extraction with benzene. The resulting resin is a viscous mass.

Hydrogenated naphthalenes have also been utilized in condensations with aldehydes, forming products which can be incorporated with linseed oil and turpentine in varnish manufacture.<sup>18</sup> Using phosphorus pentoxide as a catalyst, tetrahydronaphthalene will condense with paraformaldehyde to form a light-colored resin, and a viscous oil, the latter probably ditetrahydronaphthalene.<sup>19</sup> The use of inorganic acids in place of phosphorus pentoxide will produce more resin and less oil.

Morgan and Harrison<sup>20</sup> have made resins by condensing acenaphthene with formaldehyde. In experimental work 26 g. of acenaphthene and 5 g. of paraformaldehyde were dissolved in 450 cc. of glacial acetic acid at 25°C. Into this was stirred a mixture of 4.2 cc. of concentrated sulphuric acid and 9 cc. of glacial acetic acid. The liquid quickly developed a light blue color, and in a few minutes a white solid began to precipitate. After 5 days the solid was washed with water and dried (yield 25 g.). The resin had a melting point of 126-128°C. and was soluble in chloroform, benzene, and carbon tetrachloride, but insoluble in alcohol. It was found that fluorene and indene produced resins when similarly treated. 4-Chloroacenaphthene, when treated with formaldehyde as above, produced a resin, and also when heated with alkali it produced tarry material (m.p. 210-215°). In experiments by Lorrimer,<sup>21</sup> gummy products were obtained when acenaphthene, dissolved in benzene, was treated with a mixture of acetic anhydride and the reaction product of phthalic anhydride and aluminum chloride.

Indene was condensed with formaldehyde by Claasz,<sup>22</sup> as follows: A mixture of 100 parts of indene, 100 parts of formalin (30 per cent), and 5-10 parts of concentrated hydrochloric acid is boiled under reflux for 5 hours, yielding a layer of

<sup>13</sup> German P. 403,264, 1919, to Farb. vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1925, 44, 216B.

<sup>14</sup> German P. 406,152, 1919, 406,999, 1919, and 407,000, 1920, to Farb. vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1923, 44, 461B.

<sup>15</sup> German P. 387,836, 1918, to Chem. Fabr. K. Albert, G. m. b. H.; *J.S.C.I.*, 1924, 43, 797B.

<sup>16</sup> See *American Perfumer*, 1923, 18, 541.

<sup>17</sup> German P. 365,541, 1920, to Farb. vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1923, 42, 614A.

<sup>18</sup> German P. 305,575, 1917, to Akt. Ges. für Anilin-Fabr.; *J.S.C.I.*, 1921, 40, 439A.

<sup>19</sup> German P. 333,060, 1918, addition to 319,799, 1917, to Tetralin G. m. b. H.; *J.S.C.I.*, 1921, 40, 379A.

<sup>20</sup> G. T. Morgan and H. A. Harrison, *J.S.C.I.*, 1930, 49, 250T, 418T, 420T. British P. 319,444, 1928; *Chem. Abs.*, 1930, 24, 2824.

<sup>21</sup> F. R. Lorrimer, *J.A.C.S.*, 1927, 47, 212.

<sup>22</sup> M. Claasz, German P. 310,783, 1918; *J.C.S.I.*, 1920, 39, 273A.

thick, clear oil, which becomes viscous when washed and cooled. When exposed to air it acts somewhat like a drying oil.

The condensation of 1-chloronaphthalene with formaldehyde in the presence of acids was found to yield clear elastic resins useful in varnishes and in the preservation of leather.<sup>23</sup> It was also found that chloronaphthalenes will condense with themselves or with aromatic hydrocarbons if aluminum chloride or ferric chloride is used as a catalyst. These resins are soluble in oils but not in alcohol. Beer<sup>24</sup> noted that 1-chloronaphthalene or its methyl homologues, or chlorinated anthracene could be condensed with less than 10 per cent of formaldehyde in sulphuric acid at a temperature below that at which the hydrocarbon is ordinarily sulphonated. The resins were soluble and could be used as wetting, dispersing and emulsifying agents, and as solvents for fats and oils.

Bosshard and Strauss<sup>25</sup> observed that naphthalene will condense when it is heated with dehydrated oxalic acid and aluminum chloride at 100°C. Treatment of the reaction product with hydrochloric acid, and subsequent steam distillation to remove excess naphthalene yielded a brittle, reddish brown resin (m.p. 95°) resembling colophony.<sup>26</sup> The use of ferric chloride instead of aluminum chloride resulted in a blackish brown pulverulent mass (m.p. 180°C.). These resins were used in varnishes and as impregnating agents.

Similarly, a condensation of naphthalene is effected by heating it with glycollic acid and phosphorus pentoxide.<sup>27</sup> The reaction is carried out by heating this mixture under pressure for 15 hours at 130-170°C., allowing carbon dioxide to escape from the apparatus from time to time. Steam distillation of the reaction product removes unchanged naphthalene and leaves behind a yellow resin (m. p. 80-85°C.) resembling shellac. Aromatic hydrocarbons may be converted into resins by first decomposing them with sulphuric acid using phosphorus pentachloride or sulphur dichloride as a catalyst, and then condensing the products directly with polyhydric alcohols, e.g., glycerol.<sup>28</sup>

Anthracene and phenanthrene, in the presence of aluminum chloride in aromatic hydrocarbons (benzene, toluene or m-xylene), undergo autocondensations, and also condensations with the aromatic hydrocarbons.<sup>29</sup> In the autocondensations, very active hydrogen is released which causes the formation of low-melting tarry by-products. However, if dry oxygen is passed through the reaction mixture, the active hydrogen is oxidized, and the resins obtained have higher melting points.

Resins have been formed by condensing benzene, ethylbenzene, isopropylbenzene or butylbenzene with a symmetrical ethylene dihalide using aluminum chloride as catalyst.<sup>30</sup>

In the methylation of xylene to form durene, pentamethylbenzene and hexamethylbenzene, Smith and Dobrovolsky<sup>31</sup> found that the synthesis of hexamethylbenzene was hindered by the formation of dark tars from condensed rings and from the decomposition of hexamethylbenzene. Red, tarry material was obtained<sup>32</sup> in an attempt to convert pentamethylbenzene into hexamethylbenzene and 1,2,3,4-

<sup>23</sup> German P. 332,334 and 332,391, 1918, to Akt. Ges. für Anilin-Fabr.; *J.S.C.I.*, 1921, 40, 358A

<sup>24</sup> O. L. Beer, British P. 362,016, 1930; *Chem. Abs.*, 1933, 27, 1112.

<sup>25</sup> H. Bosshard and D. Strauss, German P. 380,577, 1920, to Elektrochem. Werke G. m. b. H.; *J.S.C.I.*, 1924, 43, 433B.

<sup>26</sup> A Japanese acid earth has been employed in resinifying naphthalene. See K. Ishimura, *Bull. Chem. Soc. Japan*, 1934, 9, 521; *Chem. Abs.*, 1935, 29, 1704.

<sup>27</sup> H. Bosshard and D. Strauss, British P. 171,950, 1921, to Elektrochem. Werke G. m. b. H.; *J.S.C.I.*, 1922, 41, 676A.

<sup>28</sup> French P. 726,148, 1931, to Allgem. Elekt.-Ges.; *Chem. Abs.*, 1932, 26, 4970.

<sup>29</sup> A. Schaarschmidt, C. Mayer-Bogström, and J. Sevón, *Ber.*, 1925, 58, 156; *Chem. Abs.*, 1925, 19, 1570.

<sup>30</sup> French P. 743,753, 1933, to the Naugatuck Chemical Co.; *Chem. Abs.*, 1933, 27, 3789. See R. Anschütz (*Ann.*, 235, 150, 299; *J.C.S.*, 1887, 52, 150) for early work on this reaction.

<sup>31</sup> L. I. Smith and F. J. Dobrovolsky, *J.A.C.S.*, 1926, 48, 1413

<sup>32</sup> L. I. Smith and A. R. Lux, *J.A.C.S.*, 1929, 51, 2994

tetramethylbenzene (prehnite) by the action of sulphuric acid (the Jacobsen reaction).

A resinous hydrocarbon of the formula  $(C_7H_8)_n$  was obtained by Sabatier and Maible<sup>32</sup> by the dehydration of benzyl alcohol with metallic oxides at temperatures of 250-350°C. Analogous to this is the reaction of 1 volume of benzyl alcohol with 2 volumes of sulphuric acid trihydrate to form a mixture of hydrocarbons which on distillation yielded a yellow, fluorescent resin.<sup>34</sup>

#### WATER SOLUBLE PRODUCTS

The replacement of natural products by synthetic resinous substances has affected the leather industry, and tanning operations can be carried out with material obtained from the condensation of formaldehyde with either sulphonated hydrocarbons or sulphonated phenols.<sup>35</sup> These products are also useful as wetting agents.

A tanning agent was made by Schmidt<sup>36</sup> in the following manner: Naphthalene and sulphuric acid are heated together at 140°C. forming  $\beta$ -naphthalene sulphonic acid. After cooling and maintaining the temperature at 60-100°C., formaldehyde is added gradually. Then, as the mass thickens, water is added to facilitate stirring. On cooling, the product solidifies to a resinous, slightly colored, water-soluble mass. The resin can be used directly as a tanning agent, or it can be added to the difficultly soluble tanning extracts such as quebracho, chestnut, or mangrove to increase their solubility and efficiency. Kämpf<sup>37</sup> used the sulphonic acids of aromatic hydrocarbons or their condensation products with aldehydes and ketones in the preparation of spinning-baths for viscose solutions. Egner<sup>38</sup> mixed formaldehyde-naphthalene sulphonic acid condensations with dried products from the nitric acid oxidation of peat or lignite. This material tanned leather to a light color.

A water-soluble condensation product useful as a tanning agent was made by Jaeger.<sup>39</sup> Sulphonated hydrocarbons were condensed with carbohydrates and then further condensed with formaldehyde, and the product converted into the sodium salt. Hydrocarbons used in this process were crude anthracene and naphthalene, and the carbohydrates included cellulose from old sulphite paper, cotton rags or wood pulp, or soluble sugars or starches. When crude hydrocarbons are used the products are sometimes highly colored, this being an objectionable feature in some cases. The color can be removed by oxidizing the material with hypochlorites, chlorine, chromic acid or potassium permanganate.<sup>40</sup> Sulphonated hydrocarbon mixtures produced by treating crude naphthalene, or anthracene oil, are condensed with formaldehyde in a process by Moeller<sup>41</sup> to produce tanning agents. In place of sulphonated hydrocarbons a crude acid resin can be used, provided sufficient naphthalene or anthracene is added to it to use up the excess sulphuric acid in the resin.

A type of wetting or dispersing agent has been obtained by condensing

<sup>32</sup> P. Sabatier and A. Maible, *Compt. rend.*, 1908, 147, 106; *J.C.S.*, 1908, 94 (1), 713

<sup>34</sup> J. B. Sendrens, *Compt. rend.*, 1926, 182, 612; *Chem. Abs.*, 1926, 20, 1985

<sup>35</sup> The effects produced on hide substances by the condensation products of formaldehyde and sulphonic acids have been described by E. Wolesensky, *Tech. Papers, U. S. Bur. Standards*, 1926, 309, 275; *Chem. Abs.*, 1926, 20, 1535.

<sup>36</sup> O. Schmidt, U. S. P. 1,336,759, April 13, 1920; *Chem. Abs.*, 1920, 14, 1766. Canadian P. 227,609, 1923; *Chem. Abs.*, 1923, 17, 1348. Also U. S. P. 1,216,612, Feb. 20, 1917; *Chem. Abs.*, 1917, 11, 1332. Canadian P. 228,241 and 228,242, 1923; *Chem. Abs.*, 1923, 17, 1348.

<sup>37</sup> A. Kämpf, British P. 234,188 and 234,433, 1924; *J.S.C.I.*, 1925, 44, 587B

<sup>38</sup> M. Egner, German P. 420,647, 1924, to Badische Anilin- & Soda-Fabrik; *Brit. Chem. Abs.*, B, 1926, 456.

<sup>39</sup> A. O. Jaeger, U. S. P. 1,961,151, June 5, 1934, to the Selden Co.; *Chem. Abs.*, 1934, 28, 4848.

<sup>40</sup> A. O. Jaeger, U. S. P. 1,941,475, Jan. 2, 1934, to the Selden Co.; *Chem. Abs.*, 1934, 28, 1888.

<sup>41</sup> W. Moeller, U. S. P. 1,448,278, Mar. 13, 1923, to the Chemical Foundation, Inc.; *Chem. Abs.*, 1923, 17, 1902. Cf. H. Renner and W. Moeller, British P. 146,166 and 146,180, 1920; *J.S.C.I.*, 1922, 41, 150A. German P. 262,333, 1913; *Chem. Abs.*, 1913, 7, 3553.

$\beta$ -naphthalene sulphonic acid with benzoic acid and an alcohol using sulphuric acid as a condensing agent.<sup>42</sup> The product, after washing with water, neutralizing with caustic soda and precipitating with sodium chloride, is a grayish-white powder, soluble in water. Similarly, the sulphonated products of mineral oil fractions when condensed with alcohols have yielded wetting-out agents or emulsifiers.<sup>43</sup>

#### RESINS FROM REDUCTION AND OXIDATION OF AROMATIC HYDROCARBONS

**Reduction.** Although experiments under this heading would hardly be expected to lead to any resinous products, the explanation of such resin formation may be that the partially hydrogenated intermediate compounds polymerize more rapidly than they absorb hydrogen.

Naphthalene and anthracene, when hydrogenated under 190-250 atmospheres pressure at 350-490°C., yielded tetrahydro derivatives, liquids resembling benzene and high-boiling, pitchy decomposition products.<sup>44</sup> Aluminum chloride as a catalyst increased the yield of liquid, but not of pitchy products. Schroeter, Müller and Huang<sup>45</sup> found that although pure phenanthrene hydrogenates smoothly to di-, tetra- and octahydro derivatives, technical phenanthrene is converted by sodium and amyl alcohol into di- and tetrahydro compounds and a considerable portion of resinous material. Maible<sup>46</sup> observed that during the reduction of benzene and its methyl homologues to methane at 270-280°C. in the presence of nickel, a resin soluble in acetone was deposited on the catalyst. Ipatiev, Orlov and Dolgov<sup>47</sup> have done considerable work on the hydrogenation and dissociation of aromatic hydrocarbons under pressure, and have obtained, in many cases, resinous substances as by-products.

**Oxidation.** In experiments by Ono,<sup>48</sup> naphthalene was oxidized electrolytically to  $\alpha$ -naphthaquinone with the formation of small quantities of phthalic acid and some dark-brown resinous matter. The electrolysis was carried out in acid solution using lead peroxide and platinum as the positive pole. The resinous matter contained phenolic hydroxyl groups.

Fichter and Herszbein<sup>49</sup> found that electrolytic oxidation of  $\alpha$ -methylnaphthalene in sulphuric acid solution produced a resin (yield 37%). In corresponding experiments Fichter and Meyer<sup>50</sup> obtained resinous material by the electrochemical oxidation of m-xylene emulsified with sulphuric acid, and of cymene in sulphuric acid-acetone solution.

Austin and Black observed that the Tesla discharge converted benzene vapor into biphenyl, and toluene into bibenzyl.<sup>51</sup> In addition, in each case resinous products similar to shellac were formed. The resin had a deep reddish brown color and was apparently formed by condensed molecules of a phenolic type, the necessary oxygen having been derived from water molecules, since the hydrocarbons were not absolutely dry. This work was a continuation of earlier work by Aus-

<sup>42</sup> F. Felix, U. S. P. 1,833,245, Nov. 24, 1931, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 1403.

<sup>43</sup> J. Baddiley and E. Chapman, British P. 274,611, 1928, to British Dyest. Corp., Ltd.; *Brit. Chem. Abs.*, B, 1927, 841.

<sup>44</sup> H. Winter and G. Free, *Brennst.-Chem.*, 1931, 12, 451; *Chem. Abs.*, 1932, 26, 1276.

<sup>45</sup> G. Schroeter, H. Müller and J. Y. S. Huang, *Ber.*, 1929, 62, 645; *Brit. Chem. Abs.*, A, 1929, 548.

<sup>46</sup> A. Maible, *Chimie et industrie*, 1932, 28, 1263; *Brit. Chem. Abs.*, A, 1933, 152.

<sup>47</sup> V. N. Ipatiev and N. A. Orlov, *Ber.*, 1927, 60, 1963; *Brit. Chem. Abs.*, A, 1927, 1060. V. N. Ipatiev and B. N. Dolgov, *Bull. soc. chim.*, 1929, (4) 45, 950; *Chem. Abs.*, 1930, 24, 1369. N. A. Orlov, *Ber.*, 1929, 62, 710; *Brit. Chem. Abs.*, A, 1929, 549.

<sup>48</sup> K. Ono, *J. Chem. Soc. Japan*, 1921, 42, 38; *J.C.S.*, 1921, 120 (1), 334.

<sup>49</sup> F. Fichter and S. Herszbein, *Helv. Chim. Acta*, 1923, 11, 1264; *Chem. Abs.*, 1929, 23, 1896.

<sup>50</sup> F. Fichter and J. Meyer, *Helv. Chim. Acta*, 1925, 8, 74, 285; *Chem. Abs.*, 1925, 19, 1251; *J.C.S.*, 1925, 128 (1), 800.

<sup>51</sup> J. B. Austin and I. A. Black, *J.A.C.S.*, 1930, 52, 4552.

tin<sup>52</sup> and by Harkins and Gans<sup>53</sup> on the behavior of hydrocarbon vapors in the electrodeless discharge. In these experiments resinous deposits were formed but they contained no oxygen. [Formula (CH)<sub>n</sub>.] Similarly, benzene in the brush discharge yielded a resinous product (C<sub>6</sub>H<sub>4</sub>)<sub>n</sub>, in experiments by Davis.<sup>54</sup>

Fowler and Mardles<sup>55</sup> found that an electric spark passing between carbon electrodes below the surface of liquid benzene decomposed the latter with the formation of a thick yellow liquid.

The action of canal rays on hydrocarbon vapors was studied by Kohlschütter and Frumkin.<sup>56</sup> With a cathode fall of 200-400 volts, all the hydrocarbons used (benzene, naphthalene, anthracene, biphenyl, phenanthrene) formed a deposit of decomposition products on the cathode. Subsequent heating of this deposit *in vacuo* at 500°C. caused the formation of a sublimate of tar. Becker<sup>57</sup> found that decalin (C<sub>10</sub>H<sub>18</sub>) and tetralin (C<sub>10</sub>H<sub>12</sub>) both yielded drying resins when subjected to an electrical discharge in a Siemens ozone tube.

Studying the stability of hydrocarbons in an acetic acid solution of hydrogen peroxide, Charrier and Moggi<sup>58</sup> noted that benzene reacted slowly, though prolonged action under reflux yielded carbon dioxide and a yellow resin. Naphthalene reacted much more quickly, producing phthalic acid and a resin. Phenanthrene gave the quinone and then diphenic acid and a resinous material. Gelissen and Hermans<sup>59</sup> in their studies of the action of dibenzoyl peroxide on benzene and toluene obtained considerable resinous material. The resin from benzene contained carbon (80%), hydrogen (6%) and oxygen (14%). In the case of toluene the addition of aluminum chloride or ferric chloride to the reaction mixture increased the speed of the reaction and decreased the yield of resinous matter. These workers disagreed with the explanations made by Lippmann<sup>60</sup> who performed some of the primary work on this reaction. Berthelot<sup>61</sup> found that the oxidizing action of sunlight was sufficient to convert benzene into a resinous product.

In attempts to oxidize crude anthracene to anthraquinone it was discovered that phenanthrene, dissolved in nitrobenzene, yielded resinous products when oxidized with oxides of nitrogen.<sup>62</sup> Melamid<sup>63</sup> noted that the oxidation of anthracene oil (b.p. 300-350°C.) when effected with a mixture of sulphuric acid and potassium bichromate or permanganate at -20 to -15°C. using a solvent such as benzene gave a resin, and an oil which could be used in electric transformers. Rubrene (C<sub>42</sub>H<sub>38</sub>), when treated with chromic oxide oxidized to a resin, in experiments performed by Dufrasse and Enderlin.<sup>64</sup>

Experiments on the oxidation of methylbenzenes such as toluene, m-xylene, mesitylene, durene and cymene were carried out by Stephens<sup>65</sup> by bubbling dry oxygen through the dry, purified hydrocarbons in dim, diffused light at about 100°C. In every case an aldehyde and the corresponding acid were formed, and in addition a considerable quantity of a reddish brown resin.

<sup>52</sup> J. B. Austin, *J.A.C.S.*, 1930, 52, 3026

<sup>53</sup> W. D. Harkins and D. M. Gans, *J.A.C.S.*, 1930, 52, 2578.

<sup>54</sup> A. P. Davis, *J. Phys. Chem.*, 1931, 35, 3330; *Chem. Abs.*, 1932, 26, 922

<sup>55</sup> N. R. Fowler and E. W. J. Mardles, *Trans. Faraday Soc.*, 1927, 23, 301; *Chem. Abs.*, 1927, 21, 3808.

<sup>56</sup> V. Kohlschütter and A. Frumkin, *Ber.*, 1921, 54, 587; *Chem. Abs.*, 15, 2623.

<sup>57</sup> H. Becker, *Wiss. Veröffent. Siemens-Konzern*, 1929, 8 (2), 199; *Chem. Abs.*, 1930, 24, 1803.

<sup>58</sup> G. Charrier and A. Moggi, *Gazz.*, 1927, 57, 736; *Brit. Chem. Abs.*, 1928, 51.

<sup>59</sup> H. Gelissen and P. H. Hermans, *Ber.*, 1925, 58, 285, 478; *Chem. Abs.*, 1925, 19, 1564, 1858.

<sup>60</sup> E. Lippmann, *Monatsh.-Chem.*, 1886, 7, 521; *J.C.S.*, 1887, 52, 151.

<sup>61</sup> M. P. E. Berthelot, *Ann. chim. phys.*, 1900, (7) 19, 150; *J.C.S.*, 1900, 78 (2), 329.

<sup>62</sup> M. A. Il'insky, B. V. Maksorov, and N. V. Elagin, *J. Chem. Ind. (Moscow)*, 1928, 5, 469; *Chem. Abs.*, 1928, 22, 3888.

<sup>63</sup> M. Melamid, *British P.* 143,193, 1920; *J.S.C.I.*, 1921, 40, 173A.

<sup>64</sup> C. Dufrasse and L. Enderlin, *Bull. soc. chim.*, 1932, (4) 51, 132; *Brit. Chem. Abs.*, 1932, 507. For information on structure and preparation of rubrene see C. Moureu and C. Dufrasse, *Z. physik. Chem.*, 1927, 130, 472; *Chem. Abs.*, 1928, 22, 779.

<sup>65</sup> H. N. Stephens, *J.A.C.S.*, 1926, 48, 1824.

Vollman<sup>66</sup> observed that tetrahydronaphthalene on exposure to the air becomes yellow and to a certain degree resinifies like turpentine. Wittig and Leo<sup>67</sup> in studies on hexasubstituted ethanes noted that *p,p'*-bis(diphenylmethyl)diphenylmethane and the corresponding substituted ethane both formed resins when oxidized by contact with the air. The fulvene of  $\beta$ -ionone is a viscous, orange-colored hydrocarbon of the formula  $C_{18}H_{24}$ . On exposure to the air the compound absorbs oxygen and forms a resinous mass.<sup>68</sup>

#### RESINS FROM REDUCTION AND OXIDATION OF PHENOLS

**Reduction.** In experiments on the pyrogenous dissociation of aromatic compounds under pressure of hydrogen and in presence of catalysts Ipatiev and Orlov<sup>69</sup> observed that after four hours heating at 500-550°C. under 60 atmospheres of hydrogen, diphenyl ether yielded a little benzene, 3 per cent phenol, and about 30 per cent of a non-volatile, viscous, black resin, the remainder being unchanged material. In the presence of alumina at 480°C., the reaction yielded 15 per cent benzene, 9 per cent phenol, but no resin. When heated under the same conditions but with a mixture of aluminum and cupric oxides, neither phenol nor *o*-cresol gave any resin. Some 20 per cent of the phenol employed was reduced to benzene. Catechol, however, yielded 75 per cent phenol, 10 per cent benzene and 15 per cent of a brittle brown resin. Working with Dolgov, Ipatiev<sup>70</sup> isolated several crystalline compounds and a considerable amount of resin from the reduction of  $\beta$ ,  $\beta$ -dihydroxydinaphthylmethane under 100 atmospheres of hydrogen in the presence of nickel at 250°C.

**Oxidation.** The rapid discoloration by air of alkaline solutions of phenols is a commonplace observation, and the well-known estimation of oxygen in gas analysis is based on the extreme rapidity with which pyrogallol absorbs oxygen under such conditions. Photograph development is based on a similar property of hydroquinone. Fischer<sup>71</sup> and co-workers, in particular, have made a study of these reactions and found that the products formed could be readily obtained as resins useful for a variety of purposes, such as ingredients in paint and varnish preparations. For instance, dissolving phenol in concentrated aqueous ammonia solution and treating with air, using copper as a catalyst, a black solution was obtained which dried to a viscous syrup and finally to a varnish-like product.

Pummerer<sup>72</sup> oxidized phenol or its homologues in alkaline solution with potassium ferricyanide, or in acetic acid solution with lead dioxide, or with ferric chloride. The brown, resinous products so obtained were further polymerized by treatment with alkalis, acids, or heat. Reduction or acylation of these products improved their color and rendered them insoluble in alkali.

By bubbling moist air through cresols or xlenols for about 10 hours at 150-170°C. in the presence of traces of manganese dioxide or ferric chloride, resinous substances have been obtained.<sup>73</sup> Unchanged material is removed by steam distillation. Both the duration of the heating and the reaction temperature affect the quality of the resulting products, which are usually dark brown to black masses, ranging in consistency from soft to hard brittle resins. The softer products are converted into highly lustrous, hard and brittle resins on further heating. The resins are soluble in dilute caustic soda solution but are not soluble in sodium carbonate. They are soluble in some organic solvents, e.g., ether, alcohol, acetone

<sup>66</sup> H. Vollman, *Farben-Ztg.*, 1919, 24, 1689; *Chem. Abs.*, 1920, 14, 357.

<sup>67</sup> G. Wittig and M. Leo, *Ber.*, 1928, 61, 854; *Chem. Abs.*, 1928, 22, 3978.

<sup>68</sup> E. P. Kohler and J. Kable, *J.A.C.S.*, 1934, 56, 2758.

<sup>69</sup> V. N. Ipatiev and N. A. Orlov, *Ber.*, 1927, 60, 1963; *Chem. Abs.*, 1928, 22, 396.

<sup>70</sup> V. N. Ipatiev and B. N. Dolgov, *Bull. soc. chim.*, 1929, (4) 45, 950; *Chem. Abs.*, 1930, 24, 1369.

<sup>71</sup> F. Fischer and U. Ehrhardt, *Ges. Abhandl. Kennt. Kohle*, 1919, 4, 237; *Chem. Abs.*, 1921, 15, 3635.

<sup>72</sup> R. Pummerer, *British P.* 165,408, 1921; *Chem. Abs.*, 1922, 16, 506.

<sup>73</sup> German P. 357,756, 1920, to Chem. Werke Grenzach A.-G.; *J.S.C.I.*, 1922, 41, 948A.

and benzene but are insoluble in cold turpentine. The softer resins are readily soluble in fatty oils but the hard resins go into solution very slowly. The resinification is thought to be brought about by oxidation of the alkyl groups of the phenols and subsequent polymerization of the resulting intermediate reaction products, this second reaction occurring either among the intermediate products themselves or with unchanged phenols.

Bunge<sup>74</sup> prepared resins by oxidizing phenols in primary monohydric alcohols using as catalysts palladium, platinum or the salts of vanadium. As an example, phenol in methyl alcohol is heated under 20 atmospheres of oxygen in an autoclave using an alkaline solution of a vanadium salt as catalyst.

Magidson and fellow-workers<sup>75</sup> obtained resinous material when oxidizing phenol with sodium peroxide in sulphuric acid solution in an attempt to produce pyrocatechol and hydroquinone. The use of hydrogen peroxide to oxidize anisole to guaiacol caused the formation of much resinous material, formed apparently from the condensation of the guaiacol under the influence of the oxidizing agent.

Voss<sup>76</sup> found that certain oily condensation products could be converted into resins by oxidation. Passing air or oxygen at temperatures of 160-190°C. into the condensation products of phenol and benzyl chloride, naphthalene and benzene chloride, and tricresol and xylyl chloride, he obtained brown resins, suggested for lakes, insulators and varnishes.

Cresol is used as an absorption liquid for solvent recovery in the Brégeat system.<sup>77</sup> Its prolonged use however results in the contamination of the cresol with considerable amounts of resin, thereby lowering the efficiency of the cresol.<sup>78</sup> It was found that this resinification was caused by the presence of volatile acids, industrial dust and various peroxides. It was observed by Triebs<sup>79</sup> that the resinification of phenols by air-oxidation is catalyzed by the presence of iron, lead, bismuth, cobalt, nickel, copper or aluminum. He also noted that cresol resin so obtained contains less oxygen than the original cresol, because of the formation of water in the oxidation.

Goldschmidt, Schulz and Bernard<sup>80</sup> obtained a brown resin (30% yield) by oxidizing o-cresol with lead dioxide in a mixture of moist ether and acetic acid at -10°C. Analysis and molecular weight determinations indicated the formula  $C_{11}H_{10}O_2(OH)$ . The presence of the hydroxyl group was shown by the solubility of the resin in caustic soda and by methylation with dimethylsulphate. In an attempt to synthesize a perhydrobenzophenanthrene, Schrauth and Görig<sup>81</sup> obtained a resin as the result of oxidizing with phosphorus pentoxide a mixture of phenol and o-cyclohexyl-cyclohexanol. The resin was dark brown in color and solidified to a glassy, transparent mass. When applied to wood, it formed a lac-like coating.

#### ELECTROLYTIC OXIDATION

Bartoli and Papasogli<sup>82</sup> on electrolyzing solutions of phenol in potassium and sodium hydroxides with coke, graphite and platinum electrodes, obtained an acid

<sup>74</sup> F. C. Bunge, German P. 582,728, 1933; *Chem. Abs.*, 1934, 28, 918.

<sup>75</sup> O. Y. Magidson, E. Y. Porozovska and N. E. Seligsohn, *Trans. Sci. Chem.-Pharm. Inst. (Moscow)*, 1923, 6, 23. O. Y. Magidson and N. A. Preobrazhensk, *ibid.*, 1926, 16, 65; *Chem. Abs.*, 1928, 22, 3884; 1929, 23, 1630.

<sup>76</sup> A. Voss, German P. 400,312, 1922, to Farb. vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1925, 44, 216B.

<sup>77</sup> J. H. Brégeat, British P. 150,654, 1920; *J.S.C.I.*, 1920, 39, 734A. U. S. P. 1,613,218, Jan. 4, 1927. *Chem. Abs.*, 1927, 21, 617.

<sup>78</sup> Brégeat A.-G.; *Chem. Ztg.*, 1927, 51, 101; *Chem. Abs.*, 1927, 21, 2038; *Brit. Chem. Abs. B.*, 1927, 239. R. Blochmann, *Chem.-Ztg.*, 1925, 49, 835. *Chem. Abs.*, 1926, 20, 80.

<sup>79</sup> W. Triebs, *Brennst.-Chem.*, 1933, 14, 81; *Chem. Abs.*, 1933, 27, 3803.

<sup>80</sup> S. Goldschmidt, E. Schulz and H. Bernard, *Ann.*, 1930, 478, 1. *Chem. Abs.*, 1930, 24, 2117

<sup>81</sup> W. Schrauth and K. Görig, *Ber.*, 1923, 56, 2024. *Chem. Abs.*, 1924, 18, 683

<sup>82</sup> A. Bartoli and G. Papasogli, *Gazz. chim. ital.*, 1884, 14, 103, *Ber.*, 1884, 17, 572R.

having the composition  $C_7H_6O_4$  (m.p.  $93^\circ\text{C}$ ). With retort coke as the positive electrode an extensive decomposition of phenol occurred and a resin was formed. Electrolysis of an emulsion of symmetrical-m-xylol in 2*N*-sulphuric acid, and also in acetone yielded m-xyloquinone and a resin. The latter was obtained in larger yield when an o-xylene solution of the xylol was treated similarly.<sup>83</sup> In a high vacuum this resin yielded a fraction corresponding in composition to a dixylenol ( $C_{12}H_{10}O_2$ ). Electrochemical oxidation of thymol also yielded some resin.<sup>84</sup>

#### OXIDATION UNDER PRESSURE

A more extensive investigation of oxidation of phenols to resins was made by Fischer and Schrader,<sup>85</sup> by using air under 45 atmospheres pressure. They were seeking to obtain substances similar to phenol-aldehyde resins from the phenols of low temperature tar without the addition of formaldehyde. The bodies obtained consisted partly of insoluble condensation material and partly of degradation product. Under some conditions fairly clear resinous substances were obtained, the color being dependent on the temperature and concentration of the mixture. Phenol at  $100^\circ\text{C}$ . in a 2.5*N*-caustic soda solution yielded a considerable quantity of brown resinous material, though less at  $150$ – $200^\circ\text{C}$ . The three isomeric cresols, oxidized in caustic soda solution, yielded coloring matters and degradation products but little resinous matter. The former were apparently fuchsine derivatives resulting from the condensation of cresol with aldehydes. In *N*-sulphuric acid above  $150^\circ\text{C}$ . cresol was extensively oxidized, yielding solid substances. At  $150^\circ\text{C}$ . the products were a hard lustrous orange-colored resin, soluble in benzene and alcohol, a brown substance insoluble in benzene, and small quantities of coloring matter.

Fischer<sup>86</sup> obtained yellow resinous material or asphalt-like substances by heating one molecular proportion of a phenol dissolved in an excess of 2.5*N*-caustic soda solution at about  $200^\circ\text{C}$ . and under 40 atmospheres pressure of either oxygen or air. Dilute sulphuric acid may be used instead of the alkali.

#### PRESSURE TREATMENT OF COAL-TAR PHENOLS

Fischer, Gluud and Breuer<sup>87</sup> heated low-temperature tar, its fractions boiling below and above  $300^\circ\text{C}$ ., and the phenols and neutral oils of these fractions separately under pressure in contact with steel wool in an autoclave at  $320^\circ\text{C}$ . for two successive periods of three days each. After this treatment, the tar itself and the hydrocarbons had a higher viscosity and density and a higher setting point than before. The phenols thickened more rapidly and to a greater extent than the hydrocarbons, giving pitch or asphalt-like products.<sup>88</sup>

Low-temperature tar and also the fraction distilling below  $270^\circ\text{C}$ . were subjected by Fischer and Ehrhardt<sup>89</sup> to pressure oxidation in a continuous stream of air at  $150^\circ\text{C}$ . and 40 atmospheres pressures. The product was a black, lustrous, pitchy substance partly soluble in benzene. To determine whether the hydrocarbons, as well as the phenols, were oxidized, the hydrocarbons were treated

<sup>83</sup> F. Fichter and M. Rinderspracher, *Helv. Chim. Acta*, 1927, 10, 102; *Brit. Chem. Abs. A*, 1927, 353.

<sup>84</sup> F. Fichter and A. Christen (*Helv. Chim. Acta*, 1925, 8, 322; *J.C.S.*, 1925, 128 (1), 813) obtained resinous substances in the electrolytic oxidation of 4-hydroxy-3-methoxypropenol.

<sup>85</sup> F. Fischer and H. Schrader, *Ges. Abhandl. Kennt. Kohle*, 1910, 4, 293; *J.S.C.I.*, 1921, 40, 340A.

<sup>86</sup> F. Fischer, *British P.* 149,979, 1920; *J.S.C.I.*, 1922, 41, 22A. *German P.* 347,521, 1922.

<sup>87</sup> F. Fischer, W. Gluud, and P. K. Breuer, *Ges. Abhandl. Kennt. Kohle*, 1917, 2, 222; *Chem. Abs.*, 1920, 14, 2071.

<sup>88</sup> A. Hageman and M. Neuhaus (*Braunkohle*, 1931, 30, 949; *Chem. Abs.*, 1933, 27, 2017) have stated that the tendency of tar phenols to condense under pressure increases with molecular weight.

<sup>89</sup> F. Fischer and U. Ehrhardt, *Ges. Abhandl. Kennt. Kohle*, 1919, 4, 280; *Chem. Abs.*, 1921, 15, 2713.



separately. This treatment produced a clear, limpid oil and also a reddish yellow oil which deposited solids when cooled, and when exposed to the air, dried like varnish. Thus it was indicated that the hydrocarbons were attacked but to a lesser extent than the phenols. In an oxidation carried out at 100°C. the hydrocarbons of a 270°C. fraction were scarcely attacked, whereas the phenols were extensively changed to resins and acids. It was suggested that the oxidation products of low-temperature tar can be used in paints and varnishes.

In these experiments lead oxide was found to have no catalytic effect on the oxidation, though some light was shed on the behavior of lead phenolate paints. In other studies on lead phenolates, Fischer and Ehrhardt found that crude tar oils could be oxidized with lead oxide. The oxidation products, when distilled with potassium permanganate or nitric acid, gave varnish-like materials.<sup>90</sup>

Resinous black printing colors were obtained when tar oils or tars were oxidized with oxygen under pressure using catalysts such as aluminum, iron, vanadium oxide, ferric chloride or sulphur chloride.<sup>91</sup> Kárpáti<sup>92</sup> obtained solid condensation products possessing good electric insulating properties when he oxidized under pressure tar distillates (boiling up to 230°C.) containing a high proportion of creosote.

#### BASIC LEAD PHENOLATES

A curious type of resin obtained by the action of litharge on phenols has been extensively investigated by Fischer and Ehrhardt.<sup>93</sup> Lead oxide dissolves readily in phenol with a strong evolution of heat, and, on cooling a gelatinous mass results. In water a basic lead phenolate separates, which when heated above 100°C. is transformed into a viscous product that may be drawn into threads and on cooling yields a glassy mass. These investigators attempted to utilize the product for varnishes and paints. Its films are brittle, and on protracted exposure show indications of formation of lead oxide at the surface. The resin prepared from phenol itself when applied as a coating to a surface will crystallize in the course of a few days and become worthless. Lead oxide likewise combines with cresol, parahydroxybiphenyl and the naphthols. The higher the molecular weight the less is the tendency to crystallize, and quite durable coatings were obtained from lead oxide and  $\alpha$ -naphthol. Phenols from the crude phenol-rich fraction (middle oil) of low temperature tar or coke oven tar yield products which have been found useful for protecting ironwork from rusting.

In preparing this lead compound, lead oxide is added to the phenol at about 120°C., in quantity only sufficient to give the basic compound, and the additions are made in small portions with stirring, since the resinous compound is decomposed by overheating. The product may then be thinned with benzene or solvent naphtha, or the diluent (of sufficiently high boiling point) may be present during the reaction.

Ordinary phenol (4.7 parts) and lead oxide (10.8 parts) in benzene (20 parts) yielded a solution which gave a glassy coating on drying, but in two days was cloudy, becoming crystalline and powdering readily. A cresol mixture known as liquid carbolic acid (5 parts) with lead oxide (10.8 parts) in benzene (20 parts) yielded a coating which became crystalline in the course of a few days. *p*-Hydroxybiphenyl (8.5 parts) and lead oxide (10.8 parts) gave a good coating which was unchanged for months.  $\alpha$ -Naphthol (7.2 parts) and lead oxide (10.8 parts) yielded a varnish which was slightly greenish in color after drying. The coating showed no tendency to crystallize and appeared quite resistant to weathering influences.  $\beta$ -Naphthol gave a softer product but did not darken. Phenolphthalein was unaffected by lead oxide.

Phenols from low temperature tar (b.p. 200-270°C., 200 cc.) mixed with lead oxide, (125 grams) and heated to 120°C., reacted violently causing the temperature

<sup>90</sup> F. Fischer and U. Ehrhardt, *Ges. Abhandl. Kennt. Kohle*, 1919, 4, 264; *Chem. Abs.*, 1921, 15, 3559.

<sup>91</sup> German P. 364,830, 1920, and its addition 367,495, 1920, to Rütgerswerke A.-G.; *J.S.C.I.*, 1923, 42, 614A, 731A.

<sup>92</sup> E. Kárpáti, *Chem. Rund. Mitteleuropa u. Balkan*, 1926, 3, 3; *Chem. Abs.*, 1926, 20, 3227.

<sup>93</sup> F. Fischer and U. Ehrhardt, *Ges. Abhandl. Kennt. Kohle*, 1919, 4, 257,264; *J.S.C.I.*, 1921, 40, 398A.

to rise to 140°C. The mixture was finally heated to 155°C. and subsequently thinned with 150 cc. of benzene. A rather durable varnish was obtained. Phenols boiling between 200-250°C. similarly treated with lead oxide gave a dull varnish which did not crystallize.

#### TREATMENT OF CERTAIN TARS

By extracting Russian peat with a benzene-alcohol mixture, up to 24 per cent of bitumen can be obtained.<sup>94</sup> This bitumen when treated with solvents is divided into two fractions, yellow or brown crystalline waxes soluble in light petroleum and black resins soluble in benzene. Polymerization of the resins takes place when the bitumen is heated to 180°C., yielding substances insoluble in organic solvents.

To improve the quality of tars by making them more plastic and increasing the speed of drying, the tars are treated with aldehydes and oxidizing gases using ammonia as catalyst. A similar result is obtained by incorporating with the tars a synthetic resin having an aldehydic base.<sup>95</sup>

When an intermediate distillate from gilsonite is purified with sulphuric acid and then sulphonated with fuming sulphuric acid a semi-drying viscous oil is obtained, after washing out excess acid. Mixing the oily product with linseed oil causes it to dry homogeneously rather than with the formation of a surface film.<sup>96</sup>

By treating coal-tar pitch (1000 parts) preferably containing montan wax (2 parts) with steam and hydrogen under 3-8 atmospheres pressure in presence of ferric oxide (8 parts) and chloride (5 parts), Rahmann<sup>97</sup> secured a heavy anthracene oil (80 parts) at 240-300°C., and both a yellowish wax and a reddish resin (together 370 parts) at 300-360°C. The resin and wax may be used as obtained, or may be mixed with 3 to 20 per cent of montan wax, paraffin or ceresin, and used in the manufacture of dyes, varnishes and impregnating materials.

By allowing petroleum asphalt to interact in an inert solvent with sulphuric acid or aluminum chloride, Lechler<sup>98</sup> obtained a product with greater stability and higher softening point than the original asphalt. This material was suggested for the manufacture of paints or emulsions. Tar oils, tars and pitches containing crude phenols, were used by d'Antal<sup>99</sup> to form resins by mixing them with vegetable oils or bituminous substances and heating with sulphuric acid. The resinous masses obtained in this way when mixed with fillers are said to be useful for molding articles or for structural material.

Fischer, Horn, and Küster have used lignite directly for moldings by mixing with phenols.<sup>100</sup> Lignite or lignitic brown coal, pulverized and vacuum dried, is kneaded at 80°C. with 12 per cent of its weight of cresol in a volatile solvent. Swelling occurs and when this has ceased the solvent is removed by vacuum distillation. The resulting material when pressed at about 150°C., under 4000 lbs. per square inch is named "Kohmit." It is stated to be a better electrical insulator than ordinary phenol-aldehyde resin and only slightly inferior to it in mechanical strength, and the cost of raw materials is about 10 per cent of the cost for phenol-aldehyde resin. In place of phenols the substitution of organic bases (e.g., aniline, pyridine,

<sup>94</sup> G. Stadnikov and N. Titov, *Brennstoff-Chem.*, 1928, 9, 325, 357; *Brit. Chem. Abs.* B, 1928, 882, 1929, 42.

<sup>95</sup> French P. 760,719, 1934, to Bozel-Malétra (Soc. ind. de prod. chim.); *Chem. Abs.*, 1934, 28, 4213.  
<sup>96</sup> C. N. Forrest, H. P. Hayden, and O. R. Douthett, U. S. P. 1,459,328, June 19, 1923; *Chem. Abs.*, 1923, 17, 2956.

<sup>97</sup> E. Rahmann, U. S. P. 1,853,899, April 12, 1932; *Chem. Abs.*, 1932, 26, 3371. British P. 325,810, 1928; *Brit. Chem. Abs.* B, 1930, 450.

<sup>98</sup> P. Lechler, British P. 382,842, 1932; *Brit. Chem. Abs.* B, 1933, 52.

<sup>99</sup> L. d'Antal, British P. 391,364, 1933; *Chem. Abs.*, 1933, 27, 4944.

<sup>100</sup> F. Fischer, O. Horn, and H. Küster, *Brennst.-Chem.*, 1932, 13, 468; 1934, 15, 327; *Chem. Abs.*, 1933, 27, 2014; 1934, 28, 7437.

quinoline) gave favorable results. The plasticity and strength of the material was found to be improved by the addition of small amounts of rubber. The plastic is stable, odorless, and non-melting; it is readily machined and can be used for making buttons and plates.

The neutral oils of low-temperature lignite tar, extracted with methyl alcohol, and treated with mercuric acetate at 100°C., yielded mercurous acetate, mercury and resins in experiments performed by Benthin and Ruhemann.<sup>101</sup>

Stuer and Grob<sup>102</sup> have studied the results of passing mixtures of acetylene with various gases such as ammonia, hydrogen sulphide and steam over catalysts. They found that at 350°C. steam and acetylene when passed over bog iron ore yielded a mixture of aldehydes, ketones, alcohols, phenols, and tar and resinous materials. From this mixture a good resin solvent could be obtained by fractional distillation.

By heating tar oil hydrocarbons (b.p. above 140°C.) containing 0.5 to 10 per cent of aluminum chloride with acetylene gas, Lihlenfeld<sup>103</sup> obtained viscous oils which when purified by vacuum distillation were reported to be suitable for lubrication or therapeutic purposes. By incorporating them with cellulose ethers and modifying the products by the addition of camphor, cellulose esters, oils or fillers, he obtained substances available for the manufacture of films, filaments, varnishes, insulators, adhesives, and artificial leather.

Jena<sup>104</sup> extracted a varnish resin from bituminous coal by using as solvents either methyl or ethyl alcohol or acetone. A fraction (b.p. 180-230°C.) of low-temperature bituminous coal-tar has been suggested by Ehrmann<sup>105</sup> as a source of raw material for resin and lacquer manufacture.

By extracting lignite with acetone, or other ketones, containing hydrochloric acid, staining solutions for wood are obtained. If cellulose acetate is added the solutions are said to be useful for paints or lacquers.<sup>106</sup>

An acid resin from coal-tar was used by Schuchardt<sup>107</sup> as a binder in briquettes. Liquid components were first removed from the resin by squeezing it between hot rollers and the resin was then mixed with coal dust and tar residues. Another briquette binder is made by benzene extraction of the residues from the pressure hydrogenation of coal.<sup>108</sup>

Sperr<sup>109</sup> has converted coal-tar pitch (m.p. 40°C. or over) into a paint by melting it and mixing it with solvent naphtha at 100-200°C. so that a colloidal solution is formed. The paint is said to be useful for coating iron and steel to prevent corrosion. In studies on tar acids in coal tars, Cheng and Morgan<sup>110</sup> found that the resins present in these tar acids could be extracted by treatment with caustic soda and subsequent precipitation with benzene.

Four types of resins have been isolated from the tars of wood, peat, lignite and bituminous coal:—neutral resinenes, basic resinamines, phenolic resinols and resinic acids.<sup>111</sup>

The resinenes are presumably amorphous mixtures of hydrocarbons. On oxidation with permanganate the resinenes yielded various benzenecarboxylic acids,

<sup>101</sup> G. Benthin and S. Ruhemann, *Braunkohle*, 1925, 23, 765; *Chem. Abs.*, 1925, 19, 3156.

<sup>102</sup> B. C. Stuer and W. Grob, U. S. P. 1,421,743, July 4, 1922; *Chem. Abs.*, 1922, 16, 3793.

<sup>103</sup> L. Lihlenfeld, British P. 149,317, 1920; *J.S.C.I.*, 1921, 40, 840A. British P. 149,319, 1920; *Chem. Abs.*, 1921, 15, 419.

<sup>104</sup> E. Jena, German P. 386,708, 1921; *J.S.C.I.*, 1924, 43, 641B.

<sup>105</sup> K. Ehrmann, *Brennst.-Chem.*, 1929, 10, 405; *Chem. Abs.*, 1930, 24, 5136.

<sup>106</sup> C. Ehrenberg, H. Wiederhold, C. Krug, M. G. Holstboer and K. Fischer, German P. 422,739, 1921, to Studienges. f. Ausbau der Ind.; *Brit. Chem. Abs. B.*, 1926, 414. See also O. Kiebs, *Teer u. Bitumen*, 1929, 27, 273; *Chem. Abs.*, 1929, 23, 5030.

<sup>107</sup> G. Schuchardt, German P. 376,730, 1921, to Ges. für Teerverw. in. b. H.; *J.S.C.I.*, 1923, 42, 968A.

<sup>108</sup> German P. 568,758, 1930, to Ges. für Kohlentechnik; *Chem. Abs.*, 1933, 27, 2774.

<sup>109</sup> F. W. Sperr, Jr., U. S. P. 1,275,778, Aug. 13, 1918; *Chem. Abs.*, 1918, 12, 2137.

<sup>110</sup> Y. C. Cheng and J. J. Morgan, *Gas Age Record*, 1927, 59, 737, 748, 779, 815, 851; *Chem. Abs.*, 1927, 21, 3264.

<sup>111</sup> G. T. Morgan, *J.S.C.I.*, 1928, 47, 131T; 1932, 51, 67T.

e.g., mellitic,  $C_6(COOH)_6$ , mellophanic 1,2,3,5- $C_6H_2(COOH)_4$ , and phthalic acid. The resinamines are amorphous solids insoluble in ether but soluble in alcohol and in dilute mineral acids. They consist of various nitrogen-containing substances. The resinols are amorphous solids of a phenolic nature (m.p. 100-160°C.) amounting to about 3 per cent of the weight of the original tar. The resinoic acids are of a stronger acid nature than the resinols and are soluble in aqueous sodium bicarbonate. In general the resins of low-temperature coal-tar are pale yellow to brown amorphous powders. They are of high molecular weight and are soluble in many organic solvents. Evaporation of such solutions leaves the resins behind as hard, transparent films. The resins furnish wood stains of even tone without raising the grain of the wood.<sup>112</sup>

Morgan<sup>113</sup> and others recovered resins from low temperature coal-tar by first extracting the tar with a solvent such as ether or benzene and then precipitating the resin with petroleum ether or by evaporation of the solvent. These resins were used in lacquers and molded articles.

<sup>112</sup> Considerable resinous material has been found in low-temperature tar from Utah coal. See R. L. Brown and B. F. Branting, *Ind. Eng. Chem.*, 1928, 20, 392. R. L. Brown and R. N. Pollock, *ibid.*, 1929, 21, 234.

<sup>113</sup> G. T. Morgan, F. S. Sinnatt and D. D. Pratt, British P. 331,542, 1929; *Chem. Abs.*, 1931, 25, 224. G. T. Morgan and D. D. Pratt, British P. 318,116, 1928, and 327,979, 1929; *Chem. Abs.*, 1930, 24, 2278, 5173.

# Chapter 13

## Phenol-Aldehyde Resins

### I. Historical

Condensation of phenols with aldehydes yields a large number of products of various properties. Some are crystalline, others are amorphous or resinous. This discussion concerns the resinous bodies only and includes a historical sketch of some of the early investigations of these resins, and of the development work which resulted in making phenol-aldehyde resinous products commercially successful.

**Salicylic Acid.** An insoluble resinous body was obtained by Gerhardt<sup>1</sup> as early as 1853 by dehydrating sodium salicylate with phosphorus oxychloride. The course of the reaction is indicated as follows:



Gerhardt observed that the resin was affected by aqueous caustic potash. Schroder, Prinzhorn and Kraut,<sup>2</sup> in 1869, found that the dehydration of sodium salicylate with phosphorus oxychloride produced a resin which was insoluble in water, alcohol and ether and which when treated with caustic potash could be hydrolyzed to yield salicylic acid.<sup>3</sup> Velden<sup>4</sup> showed that salicylic acid in the presence of sodium amalgam and acid forms hydroxybenzyl alcohol by reduction and then by dehydration becomes a saliretin body. Baekeland<sup>5</sup> also has shown that resinification of this character occurs when salicylic acid is reduced at the cathode by electrolysis.

By condensing salicylic acid with gallic acid Doebner<sup>6</sup> obtained a white amorphous powder which was recommended as an antiseptic. An antiseptic which readily gives off formaldehyde and ammonia was also produced by Speyer<sup>7</sup> from naphthol or polyphenols like resorcinol or pyrogallol and an excess of ammonia and of formaldehyde. This gave an insoluble powder.

**Baeyer's Work.** Any discussion of the resinous condensation products of aldehydes and phenols, lacking reference to the work of Baeyer in 1872 would be incomplete. At this early date Baeyer<sup>8</sup> announced that the reaction between phenols and aldehydes is a general one. He noticed that oil of bitter almonds (benzaldehyde) united with pyrogallallic acid on heating in a manner resembling that of phthalic acid. A colorless resinous substance associated with a red oxidation product was obtained. The colorless resin was formed immediately in the cold when pyrogallallic acid in hydrochloric acid was mixed and well agitated with oil of bitter almonds and hydrochloric acid. Resorcinol and oil of bitter al-

<sup>1</sup> C. F. Gerhardt, *Ann.*, 1853, 87, 159.

<sup>2</sup> Schroder, Prinzhorn and K. Kraut, *Ann.*, 1869, 150, 1.

<sup>3</sup> An octa- or nona-salicylosalicylic acid may be formed. The probable linking of the chain is according to the formula  $\text{HO}-\text{C}_6\text{H}_4\text{COO}-(\text{C}_6\text{H}_4\text{COO})-\text{C}_6\text{H}_4\text{COOH}$ . See F. Beilstein and F. Soelheim, *Ann.*, 1861, 117, 87. Also L. V. Redman, A. J. Weith and F. P. Brock, *Ind. Eng. Chem.*, 1914, 6, 3. E. Drabble and M. Nierenstein, *Biochem. J.*, 1907, 2, 96. *Chem. Abs.*, 1907, 1, 1146, noted similarities between resin-like constituents of cork, and salicylic acid condensation products.

<sup>4</sup> R. v. d. Velden, *J. prakt. Chem.*, 1877, (2) 15, 164; *Jahresber.*, 1877, 5, 337.

<sup>5</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1912, 4, 737.

<sup>6</sup> O. Doebner, *German P.* 94,281, 1896; *Chem. Zentr.*, 1898, 1, 299.

<sup>7</sup> A. Speyer, *German P.* 99,570, 1897; *Chem. Zentr.*, 1898, 1, 402.

<sup>8</sup> A. Baeyer, *Ber.*, 1872, 5, 25, 280, 1094.

monds react in like manner when concentrated sulphuric acid is added gradually to a mixture of them. Thickening occurs and after purification a red resin is obtained. The resin dissolves in concentrated sulphuric acid, forming a water-soluble substance.

When acetaldehyde was added to a mixture of concentrated sulphuric acid and phenol, Baeyer found the mixture to thicken and on the addition of water to yield a white sticky substance. This was soluble in caustic potash affording a violet-colored solution. Aldehyde-ammonia dissolved in hydrochloric acid and mixed with pyrogallol acid in concentrated hydrochloric acid yielded a soft white precipitate, easily soluble in hot water. By heating the aldehyde with pyrogallol and hydrochloric acids a red substance was obtained. Chloral acted similarly to acetaldehyde.

Michael and Comey<sup>9</sup> found that equal parts of acetaldehyde and resorcinol dissolved in 3 parts of alcohol and slightly acidified with hydrochloric acid solidified on heating at 100°C. to a gelatinous mass, insoluble in the usual solvents.

**Benzaldehyde and Phenols.** The reaction between benzaldehyde and phenols was studied by Michael<sup>10</sup> and found to result in various resinous bodies. Phenol and benzaldehyde in alcoholic solution, in the presence of a trace of hydrochloric acid, did not react in the cold but on heating for several hours yielded a resin. Orcinol, resorcinol and pyrogallol react with benzaldehyde in the cold in the presence of hydrochloric acid with the evolution of heat. Salicylaldehyde also reacts with phenol. Resorcinol and benzaldehyde heated in a closed tube to 200°C. form a resin, but heating in open vessels does not bring about a reaction. In the presence of acids, the union takes place far more rapidly. A trace of hydrochloric acid causes the formation of a white amorphous compound. Water may replace alcohol as a diluent. On heating to boiling the aldehyde gradually unites with the resorcinol and is completely converted into a resin. To obtain the resin in pure form, Michael treated a solution of equal parts aldehyde and resorcinol in 3 parts of alcohol with a minute amount of hydrochloric acid, and, after the reaction was complete, allowed the solution to cool and filtered it from crystalline material. The filtrate was poured into water and a white resinous mass precipitated which was extracted several times with a large quantity of cold water, redissolved in a small amount of alcohol and reprecipitated by pouring into water.

All attempts to obtain this body in a crystalline form were without success. The white material remained unchanged in contact with the air when it contained considerable water, but it darkened when the water was removed. Before drying at 100°C. the resin is insoluble in boiling water but melts under it to a reddish mass. It is very soluble in alcohol, benzene, ether and glacial acetic acid. On exposure to the air it gradually takes up oxygen and is converted into a dark brown substance, decomposition taking place very rapidly when the resin is heated. The resin dissolves readily in alkalies and the solutions become discolored quickly on exposure to air. The dried resin is also soluble in alkalies. It melts with complete decomposition at a high temperature, somewhat above 300°C. Michael prepared an acetyl derivative of the resin, a white amorphous substance somewhat less soluble in alcohol and benzene than the parent resin. The acetyl compound was insoluble in alkalies in the cold. Michael found the crystalline material formed in alcoholic solution during the preparation of the resin to be the result of the action of hydrochloric acid on the resin. The activity of acids as catalysts varies with their strength, hydrochloric and sulphuric acid being most active. Phosphoric acid is somewhat less vigorous and organic acids, such as

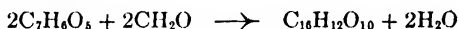
<sup>9</sup> A. Michael and A. M. Comey, *Am. Chem. J.*, 1883-1884, 5, 349.

<sup>10</sup> A. Michael, *Am. Chem. J.*, 1883-1884, 5, 338.

acetic, formic, lactic and oxalic acids, are much less active. Alkalies also were found to have a catalytic effect; caustic soda, caustic potash and potassium carbonate yielded resins of a similar character. In preparing the resins the solution should be kept as much as possible from the air when employing alkaline catalysts, as oxidation accompanied by darkening takes place.

Trzeinski<sup>11</sup> treated 3 parts by weight of  $\beta$ -naphthol and 1.5 parts of benzaldehyde in 1.5 parts of alcohol with 1 part of concentrated sulphuric acid and obtained a crystalline body, but the same procedure applied to  $\alpha$ -naphthol yielded only resinous products.

**Formaldehyde and Phenols.** Baeyer<sup>12</sup> found that methylene acetate reacted with phenol in the presence of concentrated hydrochloric acid to form a colorless resin. Ter Meer<sup>13</sup> used methylal with certain phenols and likewise obtained condensation products of resinous character which were not further investigated. However by 1890 formaldehyde was a commercial preparation and at the instigation of Emil Fisher investigations were carried out by Kleeberg<sup>14</sup> on its condensation products with phenols. Kleeberg found that formaldehyde reacts energetically with phenol, resorcinol and pyrogallol in the presence of concentrated hydrochloric acid to yield products which are insoluble in alkalies and are so difficult to purify that their composition could not be determined. With gallic acid a compound of a more definite character was produced, an acid  $C_{16}H_{12}O_{10}$ , apparently being the result of a union of two molecules each of gallic acid and formaldehyde with the elimination of water:



Kleeberg's experiments with gallic acid consisted in treating a hot aqueous solution of 20 g. of the acid with 40 cc. of commercial formaldehyde solution, concentrated hydrochloric acid being added until the solution became turbid. On cooling a small amount of a brown resin and a larger quantity of a colorless amorphous substance separated, which was particularly investigated by Kleeberg. It was found to be very difficultly soluble in all common solvents but easily soluble in fixed alkalies and aqueous ammonia. The condensation product proved to be an acid which when purified was amorphous and colorless. On strong heating it carbonized without melting.

Kleeberg mixed 10 g. of phenol with 20 cc. of a 40 per cent aqueous formaldehyde solution and added concentrated hydrochloric acid with cooling. Reaction took place with the evolution of considerable heat and a rose-red viscous mass formed which solidified on cooling. The pulverized product was extracted by boiling with water and alkalies until the color had disappeared completely. The purified product was practically insoluble in all of the common solvents and in caustic alkali solutions. On heating, it carbonized without melting. Analysis of various preparations made according to the foregoing gave no concordant results and Kleeberg concluded that the substance was a mixture of complex condensation products possessing no phenol group. It is evident that here in Kleeberg's grasp was the principle of our present-day resinoids (see Chapters 1 and 14).

Hosaeus<sup>15</sup> referred to unpublished investigations carried out by Tollens, who heated dilute formaldehyde solutions with phenol, resorcinol, pyrogallol and phloroglucinol with the addition of sulphuric or hydrochloric acid. In all cases resinous products separated which were either difficultly soluble or insoluble in all common

<sup>11</sup> W. Trzeinski, *Ber.*, 1884, 17, 499; note also *Ber.*, 1883, 16, 2335.

<sup>12</sup> A. Baeyer, *Ber.*, 1872, 5, 1094.

<sup>13</sup> E. ter Meer, *Ber.*, 1874, 7, 1700.

<sup>14</sup> W. Kleeberg, *Ann.*, 1891, 263, 253.

<sup>15</sup> H. Hosaeus, *Ber.*, 1892, 25, 3212.

solvents. Hosaeus himself treated  $\beta$ -naphthol with formaldehyde solution in the presence of acetic acid and obtained a crystalline product. Abel<sup>18</sup> investigated the reaction between formaldehyde and the naphthols and in general obtained crystalline substances. Menthol also yielded a crystalline body. Guaiacol when treated with formaldehyde and excess of guaiacol eliminated yielded a brittle yellowish mass soluble in alkalis.

Litterscheid and Thimme<sup>17</sup> treated phenol and resorcinol with monochlorodimethyl ether,  $\text{CH}_3\text{—O—CH}_2\text{Cl}$ , and obtained insoluble bodies which they described as having the appearance of porcelain and which they compared with the products obtained by Baeyer<sup>19</sup> from phenol, a formaldehyde derivative and hydrochloric acid.

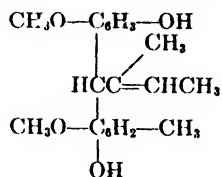
Breslau and Pictet<sup>20</sup> condensed phenol and aqueous formaldehyde in the presence of concentrated sulphuric acid, subsequently neutralizing, distilling and extracting the product with ether. The purified material (b.p. 197–200°C.) was thought by them to be methylene glycol methyl phenyl ether since the same compound was obtained by condensing potassium phenate and monochloro-dimethyl ether.

**Acids of Guaiac Resin.** An interesting research was carried out by Doebner<sup>20</sup> on the synthesis of the acids of guaiac resin (guaiacum). The three acids

found in this resin contain the radical  $\text{CH}_3\text{CH}=\text{C}\begin{array}{l} \text{CH}_3 \\ \text{OCH}_3 \end{array}$  present in tiglic aldehyde and also the guaiacol radical  $\text{—C}_6\text{H}_3\begin{array}{l} \text{OH} \end{array}$  The three acids of the

natural resin appeared to differ essentially with respect to the number of hydroxyl groups present.

Doebner mixed 5 parts of tiglic aldehyde with 9 parts each of guaiacol and cresol diluted with 20 parts of glacial acetic acid, added 2 parts of concentrated hydrochloric acid and heated the mixture for 20 minutes on a water bath. The mixture was poured into about 250 parts of strong hydrochloric acid and heated for 15 minutes longer, then poured into cold water. A brown resin separated which was purified by distillation with steam. This removed the excess of guaiacol and cresol. The resin was further purified by dissolving it in dilute caustic soda and precipitating with dilute acid. It was found to be soluble in alcohol. The purified resin was of a yellowish-brown color apparently an isomer of guaiac resin. Its constitution is represented by the following formula:



By condensing tiglic aldehyde with guaiacol and pyrogallol dimethyl ether, a somewhat similar resin was obtained. Tiglic aldehyde and dimethylpyrogallol yield a resin of the composition represented by the formula  $\text{C}_{27}\text{H}_{20}\text{O}_6$ . Doebner

<sup>18</sup> J. Abel, *Ber.*, 1892, 25, 3477.

<sup>17</sup> F. M. Litterscheid and K. Thimme, *Ann.*, 1904, 334, 49; *Chem. Zentr.*, 1904, 2, 949.

<sup>19</sup> A. Baeyer, *Ber.*, 1872, 5, 1095.

<sup>20</sup> J. Breslau and A. Pictet, *Ber.*, 1907, 40, 3784.

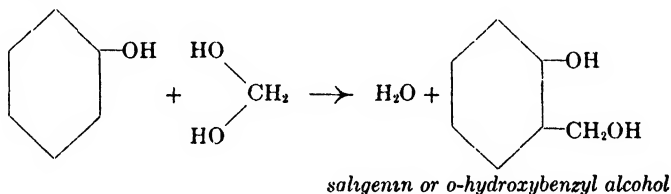
<sup>20</sup> O. Doebner, *Arch. der Pharm.*, 1896, 234, 610; *Chem. Zentr.*, 1897, 1, 167.



therefore drew the conclusion that the natural guaiac resin is a condensation product of phenols with aldehydes.

**Phenol Alcohol or Saligenin.** (Ortho-Hydroxybenzyl alcohol.) As the phenol alcohol, saligenin, plays an important role in the formation of the resinous condensation products of phenol and formaldehyde a discussion of the chemistry of this compound finds appropriate place here. Saligenin represents the simplest condensation product of phenol and formaldehyde.<sup>21</sup> Being a crystalline substance it has been prepared in a pure state. Its melting point is 82°C. Manasse in making it used as condensing agents various inorganic basic substances, namely caustic soda and caustic potash, potassium and sodium carbonate, quicklime, zinc and lead oxides, also zinc dust, sodium acetate and potassium cyanide. Lederer<sup>22</sup> used milk of lime or baryta water.

The phenol alcohol is conveniently made by dissolving phenol in somewhat more than an equivalent amount of dilute caustic soda solution. An equivalent amount of formaldehyde (40 per cent aqueous solution) is added and the mixture is allowed to stand until the odor of formaldehyde has disappeared. Then the solution is neutralized with acetic acid and extracted with ether to remove the phenol alcohols and the uncombined phenol. The latter may be removed by distillation with steam. Both the o- and p-hydroxybenzyl alcohols form. Manasse<sup>23</sup> suggested that these alcohols may be formed in one of two ways: the formaldehyde in alkaline solution may act as methylene glycol, CH<sub>2</sub>(OH)<sub>2</sub>, according to the following reaction:



or, a simple aldol transformation may take place through formation of the alcohol group by the transfer of one hydrogen atom of the phenol.

The separation of the two hydroxybenzyl alcohols was carried out by Manasse as follows: the ether extract of the crude product is dried by sodium carbonate and the solution evaporated to dryness. A yellowish oil is obtained which crystallizes after standing for a few days. The crystalline mass is treated with benzene at 50°C., which extracts o-hydroxybenzyl alcohol. From this solution the alcohol can be readily crystallized. Auwers and Daেকে<sup>24</sup> observed that p-hydroxybenzyl alcohol which has not been well purified may become resinous on standing.

Similar hydroxy alcohols are formed from certain other phenols: thymol, for example, giving a crystalline product which on being warmed in the presence of mineral acids resinifies. By treating the alcohol with concentrated sulphuric acid and diluting with water a resin is precipitated.

**Saliretin.** Piria prepared this resin by the action of dilute acids on saligenin.<sup>25</sup> Saliretin may be prepared by warming 1 part of the glucoside, salicin C<sub>6</sub>H<sub>11</sub>O<sub>6</sub>—O—C<sub>6</sub>H<sub>4</sub>—CH<sub>2</sub>OH, with 10 parts of hydrochloric acid (sp.gr. 1.25) to 80°C., precipitating with water, dissolving the precipitate in moderately dilute alcohol and

<sup>21</sup> L. Lederer, *J. prakt. Chem.*, 1894, (2) 50, 224. O. Manasse, *Ber.*, 1894, 27, 2408; U. S. P. 526,786, Oct. 2, 1894; German P. 85,588, 1894, to F. Bayer & Co.; *Chem. Zentr.*, 1896, 1, 1120.

<sup>22</sup> L. Lederer, U. S. P. 563,975, July 14, 1896. See *J.S.C.I.*, 1895, 14, 297.

<sup>23</sup> O. Manasse, *Ber.*, 1894, 27, 2408; U. S. P. 526,786, Oct. 2, 1894.

<sup>24</sup> K. Auwers and S. Daেকে, *Ber.*, 1900, 33, 3373.

<sup>25</sup> R. Piria, *Ann.*, 1845, 56, 37. See also *ibid.*, 1843, 48, 75; 1852, 81, 245; 1855, 96, 357.

precipitating the solute with brine.<sup>26</sup> Saliretin is a yellowish powder soluble in alcohol and alkalis. Moitessier<sup>27</sup> pointed out that saligenin on losing 1 molecule of water by dehydration passes over into a saliretin resin. The saliretin obtained from saligenin by Gerhardt<sup>28</sup> with sulphuric acid corresponds to the formula,  $C_{24}H_{20}O_8$ ; that is, it may be looked upon as derived from 4 molecules of saligenin by the loss of 3 molecules of water. By heating saligenin with acetic anhydride or with ethyl iodide Beilstein and Seelheim<sup>29</sup> obtained a saliretin of the composition,  $C_{20}H_{16}O_8$ , the result of withdrawal of 7 molecules of water from 8 molecules of saligenin.

Baekeland<sup>30</sup> noted that saligenin or hydroxybenzyl alcohol is very easily dehydrated and that the removal of water brings about the formation of a resinous substance. The dehydration can occur by the mere application of heat and is much hastened by strong acids and certain other chemical agents. Hence to prepare hydroxybenzyl alcohol successfully low temperatures and general careful treatment are essential. The hydroxybenzyl alcohol produced in alkaline solution by the method of Manasse is best isolated by exact neutralization with weak acids and extraction with solvents which separate it from uncombined phenol. Unless such precautions are observed the reaction may get beyond control and resinous bodies may be produced in large proportion. This is especially true when strong acids are used as condensing agents but even under such conditions Baekeland<sup>31</sup> was able to establish the presence of noticeable quantities of hydroxybenzyl alcohol.

The direct homologue of saliretin, which is methyl saliretin or homosaliretin, has properties similar to saliretin, melts at 200-205°C. and is less soluble.<sup>32</sup>

Auwers and Daecke<sup>33</sup> prepared an acetyl compound of dibromo-p-hydroxybenzyl alcohol (m.p., 112-113°C.). When this product was treated with a small amount of caustic alkali and the solution acidified a reddish-brown amorphous substance, melting at 240-250°C. with decomposition, was obtained. This substance was found to be insoluble in all common organic solvents. It formed more readily the more concentrated the solution and the longer the period of action of the alkali. A concentrated alkaline solution of the acetate in the course of a few minutes changed into a violet jelly which consisted entirely of the substance of high melting point.

The substance saliretone  $C_{14}H_{12}O_8$  is obtained by heating equal parts by weight of saligenin and glycerol for 8 hours in a sealed tube on a water bath. The contents of the tube are diluted with water and the precipitated resin is boiled with water. Evidently the reaction progresses largely to a resinous body because the yield of saliretone is given as 2½ per cent on the basis of the saligenin used.<sup>34</sup> Its melting point is 121.5°C. When saliretone is heated above 140°C., or even boiled with water for a long time, a resin is formed which has the empirical formula  $C_8H_6O$  (saliretin?), and is soluble in ether and alkalis.

**Saliretazine.** In 1894 Paal and Senninger<sup>35</sup> carried out some observations on the action of ammonia on saligenin (o-hydroxybenzyl alcohol) which are of especial interest in view of the subsequent development of commercial synthetic resins from phenol and formaldehyde. When saligenin is heated to 180-200°C. with ammonia, a basic condensation product is obtained in the form of a yellow amorphous body which is notably insoluble in acids, alkalis and various organic solvents. An

<sup>26</sup> K. Kraut, *Ann.*, 1870, 156, 124.

<sup>27</sup> Moitessier, *Jahresber.*, 1866, 677.

<sup>28</sup> C. F. Gerhardt, *Ann. chim. phys.*, 1844, (3) 7, 215.

<sup>29</sup> F. Beilstein and F. Seelheim, *Ann.*, 1861, 117, 84.

<sup>30</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1913, 5, 506.

<sup>31</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1912, 4, 737.

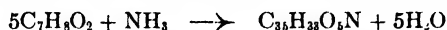
<sup>32</sup> C. Schotten, *Ber.*, 1878, 11, 784.

<sup>33</sup> K. Auwers and S. Daecke, *Ber.*, 1900, 33, 3379.

<sup>34</sup> P. Giacosa, *J. prakt. Chem.*, 1880, (2) 21, 221; Beilstein, 3rd Ed., II, 1109.

<sup>35</sup> C. Paal and H. Senninger, *Ber.*, 1894, 27, 1709.

analysis indicated the formula  $C_{35}H_{35}O_5N$ . The formation of this substance from saligenin and ammonia may be represented by the following equation:

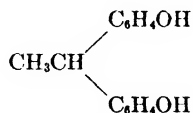


Paal and Senninger tried many solvents on this resin, including ether, alcohols, chloroform, acetone, glacial acetic acid, benzene, phenol and aniline, without finding any indication of its solubility. The substance was infusible and decomposed on heating above  $300^\circ\text{C}$ . This insoluble and infusible amorphous body is of interest in view of its bearing on Bakelite and similar infusible resinoid substances.

**Acetaldehyde and Phenol.** In the course of some experiments on the production of acetals Claus and Trainer<sup>36</sup> observed the action of acetaldehyde on phenol in the presence of hydrochloric acid gas. Because of the violence of the reaction, the following procedure was adopted:

One equivalent of acetaldehyde and 2 equivalents of phenol were dissolved in ether and cooled while hydrochloric acid gas was passed through the solution. Under these circumstances the reaction progressed quietly and after evaporating the ether and water produced by the reaction a reddish, soft, resinous mass remained. Removal of the uncombined phenol by treatment with steam yielded a hard, brittle resin. This product was insoluble in water, benzene and petroleum ether but dissolved easily in alcohol, ether, chloroform, acetone and glacial acetic acid. It was also soluble in a mixture of equal parts of benzene and ether. Efforts were made by Claus and Trainer to crystallize the resin from some of these solvents but no crystalline body could be obtained. The resin dissolved easily in aqueous caustic alkali solutions and on acidification this solution yielded a white or rose-colored precipitate which retained inorganic salts very tenaciously. The precipitated resin could not be obtained free from ash without tedious extraction with hot water or solution in ether. This resinous material began to soften at about  $100^\circ\text{C}$ , and at  $125^\circ$  was viscous. Even at higher temperatures it did not become freely fluid.

An analysis indicated that 1 molecule of the aldehyde had united with 2 molecules of phenol with the elimination of 1 molecule of water. However, instead of forming an acetal, the aldehyde had evidently joined the benzene nucleus through two hydrogen atoms to yield a compound which Claus and Trainer named ethyldenediphenol<sup>37</sup> having the formula:



Claus and Trainer also determined the action of acetaldehyde and hydrochloric acid on the naphthols.  $\alpha$ -Naphthol behaved like phenol in forming ethyldenedi- $\alpha$ -naphthol but  $\beta$ -naphthol apparently formed an acetal. This difference in behavior recalls the work of Beckmann and Dehn on furfural resins (see Chapter 24), where a very great difference was noted in the character of the reaction between furfural and  $\alpha$ - or  $\beta$ -naphthol.

**Molded Insulation by Smith's Process.** It is of interest to note that as early as 1900 phenol-aldehyde resins were proposed for making electrical insulation. Smith<sup>38</sup> made an ebonite substitute as follows:

Two volumes of paraldehyde were diluted with 1 volume of methylated spirit, 3 volumes of carboic acid (liquefied by 5 per cent of water) added and then gradually into this mixture in a closed container 3-6 volumes of fusel oil or methylated spirit saturated with hydrochloric acid were introduced. The mixture was cooled

<sup>36</sup> A. Claus and E. Trainer, *Ber.*, 1888, 19, 3004.

<sup>37</sup> See also R. Fabinyi, *Ber.*, 1878, 11, 283.

<sup>38</sup> A. Smith, U. S. P. 643,012, Feb. 6, 1900; British P. 16,247, 1899; German P. 112,685, 1899; *J.S.C.I.*, 1899, 18, 1029.

to prevent the temperature rising above 80°F. (26.7°C.). The product was poured into greased molds and allowed to set. The shaped articles were removed from the molds and dried or baked at 212°F. (100°C.). When fusel oil was employed as the vehicle for adding hydrochloric acid the product was black. It was found to be resistant to most chemical reagents. Molded articles also were treated, either before or after drying, by gradually heating in molten paraffin wax or ozokerite to 100°C. The temperature of baking reached a maximum during a period of 12-30 hours according to the thickness of the article, and was then slowly reduced. This procedure is somewhat similar to certain methods subsequently employed in cold molding. Twice the quantity of pure acetaldehyde could be used to replace paraldehyde; that is 4 volumes of acetaldehyde to 3 volumes of liquified phenol.

Polymerized formaldehyde dissolved in fusel oil which had been previously saturated with hydrochloric acid or sulphur dioxide was also recommended by Smith. The polymerized formaldehyde, 1 part, was mixed with about 5 parts of acidified fusel oil. Phenol crystals were introduced in an amount sufficient to add 50 per cent to the volume of the mixture. The composition set rapidly and could be shaped or fashioned in a manner similar to that employed with the paraldehyde composition. To any of these compositions 5-10 per cent of natural resins could be added by dissolving them in the gas-saturated fusel oil or methylated spirit before mixing. By slightly reducing the proportion of the gas-saturated alcohol the composition was obtained in a plastic condition capable of being pressed into various forms. Asbestos was used as a filler.

**Shellac Substitutes.** By 1900 a number of investigators were studying the products obtained from the reaction of phenol and formaldehyde. These previously despised resinous products were now examined with a view to seeing what could be done with them. Formerly, when it was established that reaction products could not be crystallized and possessed no definite melting point, they were discarded. Now they were studied to see what new properties they might possess. From a commercial standpoint, a shellac substitute was very attractive at this time and Blumer,<sup>30</sup> seeking such a resin, considered an hydroxy acid to be efficient as a condensing agent. He employed tartaric acid.

The following procedure was recommended: 135 parts by weight of tartaric acid are mixed with 150 parts of a 40 per cent solution of formaldehyde in a spacious jacketed vessel lined with lead. The acid is completely dissolved by heating gently and then 195 parts of commercially pure carbolic acid are introduced. Gentle heat is applied until reaction begins and from then on the heat of the reaction serves to keep the contents of the vessel in ebullition for a period of about 10 minutes. The crude resin is found floating on the surface as an oily material. This is placed in hot water and boiled after adding some ammonia. The treatment serves to eliminate the small quantity of phenol and formaldehyde present. When poured into cold water the resin at once solidifies to a white mass. Two different samples of this phenol resin gave closely agreeing results when subjected to elementary analysis, which agreed with the empirical formula,  $C_{21}H_{20}O_4$ .

Blumer carried out the condensation of  $\alpha$ -naphthol by mixing 155 parts by weight of tartaric acid with 150 parts of aqueous formaldehyde, adding 290 parts of  $\alpha$ -naphthol and permitting combination to take place. The reaction progresses violently and the product is a red resin which sets very quickly to a hard mass. As the resin does not melt in hot water it cannot be purified as phenol resin can, hence Blumer recommended that the resin be pulverized for purification purposes. The resins obtained by Blumer are stated to be suitable for the manufacture of varnishes or polishes because they are readily soluble in various solvents such as alcohol, ether and oil of turpentine. Coatings obtained with these solutions are highly resistant and possess a good luster.

<sup>30</sup> L. Blumer, German P. 172,877, 1902; British P. 12,880, 1902; British P. 6,523, 1903; *J.S.C.I.*, 1903, 22, 705; 1904, 23, 448.

**Luft's Process.** Another worker in this field in the early part of 1900 was Luft.<sup>40</sup> He also used an acid catalyst or condensing agent, recommending sulphuric, hydrochloric or oxalic acids.

For example, he suggested mixing equal parts of phenol and a 40 per cent formaldehyde solution with 0.4-0.8 part of sulphuric acid of 16-17°Bé. The mixture is heated in a vessel equipped with a reflux condenser. Violent reaction takes place yielding a white viscous mass which settles. This is collected, washed and dried. In the fresh condition the resin is plastic but when dried it ultimately becomes brittle. The resin is non-inflammable and is attacked by neither hot concentrated mineral acids nor alkalis. This property, Luft noted, would make it suitable for preparing containers for acids, alkalis and other chemicals were it not for its brittleness. Luft suggested the addition of other substances, such as camphor, rubber, glycerol or even alcohol, all of which, he stated, prevent hardening of the mass. He also remarked that mechanical operations are not without influence on the properties of the resin. A harder and very elastic mass is obtained if the resinous material is pressed in slightly warmed molds.

To render the resin transparent, Luft boiled it (after previous washing with water) while in a viscous condition with a neutralizing agent such as alkaline carbonate. The resin is then washed and dissolved in a mixture of formaldehyde and glycerol. The solution is thickened by boiling, poured into molds and dried at a temperature of about 50°C. Acetone or alcohol may also be used as a solvent. Such solutions, with the addition of coloring agents if desired, give waterproof coatings on fabrics or leather. Luft suggested drawing out the material into threads and carbonizing them for incandescent-lamp filaments.

As the resin is a non-conductor of electricity, Luft proposed its use for insulating purposes. It may also be used, he stated, as a substitute for celluloid and in the manufacture of molded articles, such as billiard balls, buttons and handles, and as an imitation amber, tortoise shell, meerschaum, vulcanite or coral and in making a kind of linoleum.

Baekeland<sup>41</sup> prepared Luft's product and found it relatively brittle and very much less tough and flexible than celluloid. It does not melt if heated, although it softens considerably. Acetone swells it and appropriate solvents extract free camphor and glycerol if these are present. In a controversy with Baekeland, Redman<sup>42</sup> discussed the Luft process, stating that the two steps which resulted in the production of Bakelite consisted in adding the basic condensing agent in certain proportions at the beginning of the reaction instead of after the reaction had proceeded for a short time in an acid solution in accordance with the Luft process, and in the use of increased heat and counter-pressure where necessary to prevent the escape of gases. Luft, according to Redman, used an acid condensing agent at the beginning of the reaction, then washed out the acid completely and added a basic condensing agent. Redman stated that Baekeland deviated from Luft's process in one step only, namely, that Baekeland added the basic condensing agent at the beginning of the reaction. Replying to this, Baekeland stated<sup>43</sup> that the Luft process involving condensation with strong acids gives products of the permanently fusible or Novolak type; or, by increasing considerably the amount of formaldehyde, produces infusible resins contaminated with products of the Novolak type unsuited for technical purposes. He said that if Luft recommended an alkali or alkali carbonate after the condensation with strong acids had taken place, this was done simply to neutralize any remaining acid difficult to wash out of the material.

<sup>40</sup> A. Luft, U. S. P. 735,278, Aug. 4, 1903; *J.S.C.I.*, 1903, 22, 1012. German P. 140,552, 1902; British P. 10,218, 1902; *J.S.C.I.*, 1902, 21, 1085.

<sup>41</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1909, 1, 151.

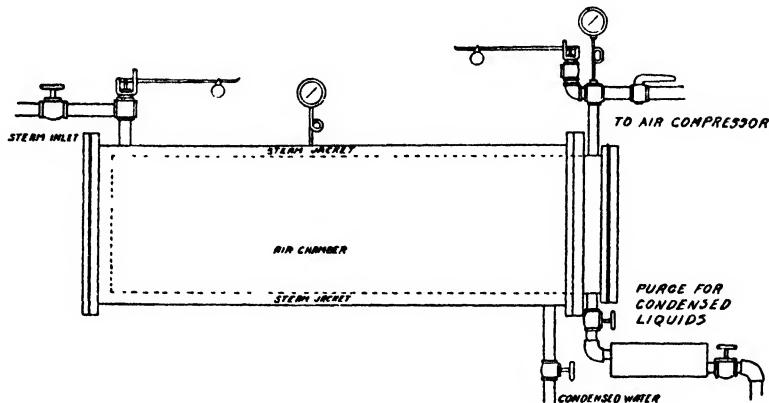
<sup>42</sup> L. V. Redman, A. J. Weith and F. P. Brock, *Ind. Eng. Chem.*, 1916, 8, 473.

<sup>43</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1916, 8, 563.

Fayolle<sup>44</sup> employed sulphuric acid as a condensing agent and added large quantities of glycerol, pitch and oils to serve as organic extending agents.

A method of preserving wood developed by Bevier<sup>45</sup> consisted in impregnating it at 150-300°F. (66-149°C.) at 100-400 lbs. pressure with a mixture of creosote, formaldehyde and resin. This treatment is followed by a hardening process which may consist in forcing milk of lime or resinate of lime into the wood.

**Cast Resins.** The next worker in this field was Story.<sup>46</sup> The process which he employed consisted in submitting phenol to the action of aqueous formaldehyde at a high temperature for a number of hours until a viscous product was obtained. This could be cast in molds and finally hardened by heating at a tem-



Courtesy Bakelite Corporation

FIG. 57.—Bakelizer. This apparatus is simply a container in which phenol-formaldehyde resins can be heated under pressure. Carbon dioxide or other gas is supplied to the bakelizer to create a pressure of several atmospheres on the resin which is undergoing hardening. Sufficient pressure is applied to counteract the tendency of the resin to become spongy due to the escape of gas when heat is applied. The apparatus has been used experimentally but finds very few commercial applications.

perature below 100°C. A mixture of 150 parts of commercial carbolic acid (95 per cent) and 30 parts of 40 per cent formaldehyde solution was recommended by Story. The reaction vessel was provided with a reflux condenser. At the end of about 4½ hours at 100°C. with continual rapid agitation the solution becomes cloudy. The heating is continued usually for a period of about 8 hours giving a product of somewhat creamy appearance. This is transferred to an open vessel and concentrated rapidly, the temperature being raised above 100°C. to drive off as much water as possible. The product should now become clear especially if the preliminary boiling has not been continued for too long a period. The viscosity of the product gradually increases and the temperature should be lowered below 100°C. after a time. Eventually a solid substance is obtained. This is hard, tough, and transparent and is a good electrical insulator. Opaque products result when the preliminary boiling is continued for a longer time, or when the concentration is conducted at a temperature below 100°C.

When shaped articles are desired the product in liquid form is poured into heated

<sup>44</sup> E. H. Fayolle, French P. 335,584, 1903; *J.S.C.I.*, 1904, 23, 195; French P. 341,013, 1904; *J.S.C.I.*, 1904, 23, 878.

<sup>45</sup> A. Bevier, U. S. P. 681,032, Aug. 20, 1901; British P. 10,297, 1900; *J.S.C.I.*, 1900, 19, 827.

<sup>46</sup> W. H. Story, British P. 8,875, 1905; *J.S.C.I.*, 1906, 23, 195; Belgian P. 210,965, 1908. Austrian P. 30,844, 1905. German P. 173,990, 1905. French P. 353,995, 1905; *J.S.C.I.*, 1905, 24, 1081. See also French addn. 9,861, 1908; *J.S.C.I.*, 1909, 28, 381.

molds and these are placed in a drying oven at about 80°C. until solidification occurs. The mass shrinks sufficiently in drying to allow the article to be withdrawn from the mold. When a very light-colored product is desired it is best, according to Story, to exclude air and light. The addition of small quantities of fatty oils, such as castor, almond, olive or rape oils, is conducive to opacity. When air is excluded during the boiling operation and fatty oil is added, the product is a white substance, which, Story stated, has the appearance of ivory or bone. The plastic material may be colored with pigments or dyes, and a black product resembling ebonite is made by the addition of pitch, lampblack, asphaltum or aniline black.

While the resin is still in a viscous state it may be dissolved in alcohol, acetone or benzene to yield a solution adapted for use as a varnish. If the solution is not too concentrated the coating will dry to a hard surface by mere exposure to the air, or may be heated to harden the resin and remove all trace of solvent. Such a varnish, according to Story, may be used for waterproofing paper and fabrics or may be employed as a vehicle in the preparation of paints. Once the resin has become hard and dry it is quite insoluble in all solvents and unattacked by acids or alkalis in the cold. Fuming nitric acid, however, disintegrates it.

The procedure of manufacture may be modified by adding the carbolic acid in small quantities from time to time to an excess of hot formaldehyde solution, or the formaldehyde solution may be added in small quantities to hot carbolic acid. A third modification consists in passing formaldehyde vapor through hot carbolic acid.

**Resins from Phenol Alcohols.** From the phenol alcohols, hard translucent resins usable as substitutes for copal, amber and shellac were produced through a process involving heating under diminished pressure.<sup>47</sup> The phenol alcohol prepared by condensing formaldehyde with phenol, cresol or menthol, is placed in a capacious receiver, melted under vacuum and heating continued at a temperature near the boiling point of the phenol alcohol so long as any water is given off. With the alcohol from cresol, the heating is continued until the mass solidifies. Solidification does not occur in the case of the o- or p-phenol alcohol,  $\text{HO}-\text{C}_6\text{H}_4-\text{CH}_2\text{OH}$ , but the end of the reaction is indicated by the appearance of copious white fumes and on cooling a hard transparent resinous mass is obtained. Saligenin yields a homogeneous, pale yellow resin resembling gum-lac, insoluble in alcohol, melting at a temperature somewhat above 110°C., and scratched by the finger nail with difficulty. The resin from p-hydroxybenzyl alcohol is somewhat similar in properties. It melts above 115°C. and has a specific gravity of 1.06. These products are soluble in hot caustic soda and are precipitated from solution by acids. Oil of camphor and terpineol are solvents. The alcohol derived from p-cresol when heated in this manner forms a transparent resin which is quite hard and heavier than water. When heated above 200°C. it softens but does not melt, and at about 300°C., begins to carbonize. The resins obtained from the cresyl alcohols are comparable in some respects with the copals.

Phenol alcohols can be condensed with certain other organic bodies to give resins of value in the plastic field. The condensation of phenol alcohols with aniline, nitrocresol, phthalic anhydride and dihydroxydiphenylmethane yields resinous masses of utility.<sup>48</sup> Condensation can be accomplished by the action of alkaline agents or by organic or mineral acids, or under the influence of heat alone, *in vacuo* or under pressure, exposed to the air or in a current of an inert gas. When condensation is carried out under pressure by heat alone, the phenol alcohol is mixed

<sup>47</sup> British P. 15,517, 1905, to Fabrique de produits de chimie organique de Laire; *J.S.C.I.*, 1906, 25, 857. German P. 159,282, 1905; French P. 350,180, 1904; *J.S.C.I.*, 1905, 24, 1244.

<sup>48</sup> Belgian P. 192,590, 1906, to Fabrique de produits de chimie organique de Laire. See also French P. 361,539, 1905; *J.S.C.I.*, 1906, 25, 939.

with the other reactant and heated in an oil bath until water vapor is evolved. The source of external heat is then removed as the temperature of the mixture rises on account of the heat of the reaction. Two successive condensations have been observed, (1) a condensation taking place while raising the temperature to about 100°C. yielding resins which are soluble in alcohol and the other usual organic solvents; and (2) a condensation taking place at a temperature above 100°C., the exact point varying with the reactants. A further evolution of water vapor occurs and a hard transparent mass more or less colored is obtained. Polymerization occurs and the solubility is dependent upon the degree of this change, the product becoming less soluble in alcohol as polymerization advances. The end product of all these condensation reactions is insoluble in alcohol.

A mixture consisting of 10 parts of phenol alcohol, 1 part of dihydroxydiphenylmethane, 15 parts of water and 3 parts of hydrochloric acid is agitated for several hours. The reaction mass is washed with water until neutral, unreacted raw materials are removed by distillation with steam, and the product is heated *in vacuo* or in the open air until the evolution of steam ceases. The product on cooling forms a transparent mass soluble in alcohol and fusing at about 100°C. Approximately the same result is obtained by dissolving 10 parts of phenol alcohol and 1 part of dihydroxydiphenylmethane in alcohol, heating *in vacuo* at a temperature of about 100°C. until the evolution of vapor ceases.

Starting with formaldehyde one procedure is as follows: 10 parts of phenol, 5-10 parts of aqueous formaldehyde (40 per cent), and 10 parts of hydrochloric acid (15 per cent) are stirred for some time and the excess of hydrochloric acid and phenol removed by washing. A plastic mass remains which is heated in the open air or under the pressure of an inert gas until, on cooling, solidification takes place rapidly. In general this requires heating for one-half hour at about 140°C. The resulting hard resin resembles amber, has a color varying from yellow to brilliant brown, and has nearly the transparency of glass. The resin is soluble in methyl and ethyl alcohols and also in caustic alkali.

A resin having approximately the same physical properties is made by carrying out the condensation in the foregoing manner, with the exception that an alkaline catalyst is used in place of hydrochloric acid. Phenol may be replaced by a homologue. For example, cresol may be condensed with formaldehyde in the presence of caustic potash.

On heating to 100°C. 2 parts of nitroresol and 10 parts of phenol alcohol dissolved in alcohol, maintaining the temperature at this point until vapor is no longer expelled and then removing the excess phenol alcohol by distillation, a resin is obtained which fuses below 100°C. and exhibits good resistance to shock. Hydrochloric acid may be added as a catalyst.

A procedure for condensing phenol alcohol with aniline consists in heating a mixture of 50 parts of phenol alcohol and 10 parts of aniline in an oil bath at about 100°C. until the evolution of water vapor ceases and test samples upon cooling show the resin to have acquired the desired consistency. The resin, which can be molded, is transparent, is scratched with difficulty by the finger nail and possesses a slight solubility in alcohol and alkalies. A more soluble resin is made by using a salt of aniline, for example the salicylate. This is condensed with the phenol alcohol by heating.

Four parts of phenol alcohol and 1 part of phthalic anhydride are dissolved in alcohol, which is removed by distillation, and the residue is heated in an oil bath at 100°C. until the evolution of water appears to cease and a test sample solidifies to a transparent resin soluble in alcohol. By prolonging the heating the product



becomes insoluble in alcohol. The following classes of substances are listed as having the power of modifying the properties of phenol alcohols in some cases presumably as a result of condensation: aldehydes, ketones, polybasic acids and anhydrides, phenols, amines and hydrocarbons.

A thorough study of the synthesis of phenol alcohols was made by Auwers<sup>40</sup> in 1907. He confirmed the results reported by previous workers that only ortho and para derivatives are obtained by the condensation of phenols and formaldehyde. His observations showed that, especially with the homologues of phenol, the para compound could be formed selectively by using the strongest alkalies such as caustic soda. Thus from p-xenol, caustic soda and formaldehyde at room temperature, the para compound was obtained in practically quantitative yield. m-Xylenol, formaldehyde and slaked lime heated carefully to 50°C. gave a fairly good yield of o-hydroxymesityl alcohol. Frequently, however, oily and resinous bodies were formed which appear to be derivatives of dihydroxydiphenylmethane, particularly with some phenols.

**Various Condensing Agents.** A "formic-aldehyde compound" was described by Stephan<sup>41</sup> in 1904 which was made in a way that may be regarded as a precursor of present methods of making phenol-formaldehyde resins. Stephan used an alkaline condensing agent (caustic potash) and formaldehyde in excess of equimolecular proportions. By heating 2 parts by weight of phenol, 1 part of caustic potash solution (40°Bé.) and 4 parts of aqueous formaldehyde to 100°C. in an autoclave, reaction occurred violently with a rise of pressure of 0.5 atmosphere. When this reaction subsided the composition was heated on a steam bath until a voluminous white powder separated on the addition of acid. The product, insoluble in water but soluble in alkali, was said to be of value as a disinfectant.

Helm<sup>42</sup> condensed aldehydes and phenols by means of amines or ammonium salts to make resinous bodies. He used 290 parts of naphthol dissolved in 150 parts of a 40 per cent solution of formaldehyde, and added 95 parts of aniline. After the reaction is over the resinous product is washed and may be used, he stated, as a substitute for gum-lac. Instead of 290 parts of naphthol, 190 parts of phenol may be used, heating to effect condensation if desired, with the formation of similar substitutes for resins or gums.

In 1903 Henschke<sup>43</sup> found that an alkaline solution of phenol, heated with formaldehyde at 100°C. in an autoclave, lost its phenolic odor. Acids precipitated from the reaction mixture a bulky, pale yellow powder, insoluble in water or chloroform, but soluble in alcohol, acetone, dilute sodium hydroxide and ammonia. It decomposed on heating or on boiling its alkaline solution. A powder intended for medicinal use was made by Sternberg<sup>44</sup> by treating wood tar with formaldehyde and hydrochloric acid. A condensation product of phenol or thymol with formaldehyde was prepared by Hildebrandt,<sup>45</sup> using hydrochloric acid as a condensing agent. Dürkopf,<sup>46</sup> Merck<sup>47</sup> and Hock<sup>47</sup> obtained condensation products of tannin and formaldehyde or hexamethylenetetramine.

Lebach<sup>48</sup> produced rapid-hardening phenol-formaldehyde resinous compositions by using inorganic or organic acid chlorides, sulphuric acid esters, aluminum

<sup>40</sup> K. Auwers, *Ber.*, 1907, 40, 2524.

<sup>41</sup> A. Stephan, U. S. P. 812,608, Feb. 13, 1906; *J.S.C.I.*, 1906, 25, 232. French P. 345,398, 1904; *J.S.C.I.*, 1904, 23, 1233.

<sup>42</sup> L. Helm, British P. 25,216, 1907; *J.S.C.I.*, 1908, 27, 412.

<sup>43</sup> F. Henschke, German P. 157,553 and 157,554, 1903; *J.C.S.*, 1905, 88 (1), 429.

<sup>44</sup> W. Sternberg, U. S. P. 761,260, May 31, 1904; French P. 329,971, 1903; *J.S.C.I.*, 1904, 23, 680.

<sup>45</sup> H. Hildebrandt, U. S. P. 876,311, Jan. 7, 1908; German P. 183,318, 1905; *Chem. Abstr.*, 1908, 2, 1500.

<sup>46</sup> E. H. Dürkopf, U. S. P. 598,914, Feb. 15, 1898.

<sup>47</sup> E. Merck, German P. 88,082 and 88,841, 1895; *Chem. Zentr.*, 1896, 2, 1016; 1, 271.

<sup>48</sup> K. Hock, U. S. P. 607,172, July 12, 1898. German P. 95,189, 1896; *Chem. Zentr.*, 1898, 1, 541.

<sup>49</sup> H. Lebach, U. S. P. 965,323, July 26, 1910, to Knoll & Co.; French P. 397,051, 1903; *J.S.C.I.*, 1909, 28, 803.

chloride and various salts as condensing agents. One procedure involves the heating of 1000 parts each of phenol and aqueous 40 per cent formaldehyde with 100 parts of crystallized sodium sulphite. A light-yellow, viscous liquid is formed which is cooled and treated with 600 parts of wheat starch and 200 parts of 20 per cent sulphuric acid. The mass is heated in a mold at 85°C. for 1-2 hours. The product is a hard lustrous insoluble article.

In another case Lebach heated phenol, formaldehyde and sodium sulphite in proportions as given above for a short time, then distilled off 500-600 parts and mixed the residual liquid with 600 parts of wheat starch. To this were added in the cold 150 parts of a mixture of 1 part sulphuric acid to 9 parts of glycerol and the product was heated in molds to 60°C. for half an hour. This gave a solid article of brilliant surface, free from pores, which could be washed with soda solution or exposed to ammonia fumes to neutralize the acid. Subsequent heating to about 100°C. improved the hardness and strength of the product. Instead of the mixture of sulphuric acid and glycerol, 10 parts of a 25 per cent aqueous solution of sodium bisulphite or 5 parts of benzoyl chloride could be used.

To avoid the problem of removal of traces of acid from the resin, Lebach proposed the use of acid salts. Small quantities of ferric chloride produce a soluble resin. Large quantities tend to promote a violent reaction and yield an insoluble resin. Ammonium chloride, sulphate and nitrate, potassium carbonate and bisulphate, and sodium sulphite were also recommended. In an example of their use, 500 parts of commercial cresol from which o-cresol has been removed, 370 parts formaldehyde and 10 parts of ammonium chloride are heated to boiling until a colorless oil separates. When separation ceases a vigorous current of steam is blown through the mass to remove excess cresol and any uncombined aldehyde. After heating for about an hour a further addition of 10 parts of ammonium chloride is made and the heating continued until a white, brittle, resinous mass is obtained on cooling a sample. The product is washed thoroughly with hot water.

In another case 500 parts of cresol, 400 parts of formaldehyde and 20 parts of sal ammoniac are heated at water-bath temperature until separation of an oil is complete, then toluene vapor is blown through the batch. In this way formaldehyde and cresol are removed. When the mass becomes cloudy the introduction of toluene vapor is stopped. On removal of traces of toluene, *in vacuo* for example, a clear transparent resin soluble in alcohol results. Various fillers may be added to the resinous composition and the aqueous formaldehyde may be replaced by hexamethylenetetramine.<sup>90</sup>

Grognot<sup>91</sup> attempted to minimize the violence of the reaction between phenol and formaldehyde in the presence of hydrochloric acid by adding glycerol. He first treated glycerol with formaldehyde in the presence of hydrochloric acid, and subsequently condensed the reaction product with phenol. A recommended procedure is the following: 2 parts by weight each of glycerol and formaldehyde are mixed and 0.3-0.4 part of hydrochloric acid (21-22°Bé.) are added. The mixture is heated until a slight ebullition occurs and reaction progresses spontaneously thereafter without external heating. When the reaction has subsided, heat may be applied for 1 or 2 hours, avoiding vigorous boiling. The mixture is cooled to 80°C. and 2 parts by weight of phenol crystals are added. Reaction takes place without further heating and is accompanied by a slight ebullition. The resin, which separates as a viscous oily layer, is washed and dried, then heated to about 150°C. until a test sample shows a hard, brilliant bead. Volatile liquids<sup>92</sup> can be added to moderate the reaction.

<sup>90</sup> British P. 28,009, 1907, to Knoll & Co.; *J.S.C.I.*, 1908, 27, 908. French P. 395,657, 1908; *J.S.C.I.*, 1909, 28, 483. Belgian P. 204,811, 1907; German P. 219,209, 1907. British P. 27,096, 1908; *J.S.C.I.*, 1909, 28, 843. British P. 6430, 1911; *J.S.C.I.*, 1912, 31, 399.

<sup>91</sup> L. Grognot, U. S. P. 906,219, Dec. 8, 1908; French P. 390,713, 1907; *J.S.C.I.*, 1908, 27, 1122.

<sup>92</sup> British P. 16,528, 1908, to Les produits chim. de Croissy, Ltd.; *J.S.C.I.*, 1909, 28, 99; French P. 392,978, 1907; *Chem. Abs.*, 1910, 4, 2748; German P. 210,012, 1907.

# Chapter 14

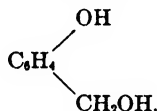
## Phenol-Aldehyde Resins

### II. Theoretical. Constitution.

Many large industries have resulted from the observation that phenol-formaldehyde products can undergo chemical transformation under the stress of temperature and pressure to form insoluble and infusible materials. Moreover, the nature of the chemical reactions involved has been the subject of considerable study, and, accordingly, the literature abounds in speculations and controversies concerning the structures of the substances involved, and the mechanism of the changes taking place. A number of noteworthy experimental investigations have been carried out, but the data which have been obtained serve largely to demonstrate the complexity of the problem rather than to provide its solution. A large number of compounds have been isolated from the condensation product. These are generally assumed to be intermediates in the resin formation, and theories concerning the structures of the resinoids<sup>1</sup> are arrived at through a consideration of the possible fates of these intermediates. Often the speculative structures are at variance with analytical data, chemical properties or physico-chemical evidence.

It has become well established that a change of catalyst may produce variation in the ease with which individual intermediates can be isolated. Therefore it appears that the course of the resin-forming reaction is determined at least in part by the nature of the catalyst. At any rate, a different set of isolable intermediates is obtained through the use of *acidic* condensing agents from the compounds produced in the presence of *alkali*. Likewise the properties of the less highly condensed resins depend upon the catalyst employed, and it is reasonable to suppose that such divergences have their source in structural differences.

Since there is no universally accepted scheme of descriptive names for the phenol-formaldehyde condensation products, their subdivision into (1) soluble-fusible resins and (2) insoluble-infusible resins is regarded as sufficiently comprehensive for the purposes of this chapter. The products of the initial stages of phenol-formaldehyde resin formation fall into the former class, and the final stage into the latter. This scheme is not intended to ignore the possible existence of a soluble infusible resin, or an insoluble fusible resin, but these are types which are seldom encountered. The term saliretin is generally accepted for those substances obtained by the action of heat on individual phenol alcohols. A typical phenol alcohol is o-hydroxybenzyl alcohol (*saligenin*),



<sup>1</sup> The term "resinoid" is here used in the sense of a synthetic resinous substance in the stage of highest stability and infusibility. This is the meaning of the designation in many of Baekeland's publications. See M. Koebner, "Brit. Plastics Year Book," 1934, 67, for general discussion of related topics.

The saliretins are the result of intermolecular condensation with elimination of the elements of water, and belong to the soluble fusible class (the Növolaks of Baeke-land).

The main line of approach to the many problems associated with resin formation is an attempt to carry out a particular condensation under as mild conditions as possible, to eliminate the unchanged reactants, to isolate chemical compounds from the condensed residue, and if possible to identify them. Mention should be made of the two chief methods which have been employed for the isolation of these compounds, viz., solvent extraction and distillation. To a limited extent degradation products of the final resins have been obtained and examined. It is relatively simple to study substances produced by condensing formaldehyde with a phenol which gives a minimum number of initial products. To elaborate this scheme: phenol, m-cresol and sym-m-xlenol are the three phenols most prone to resin formation. They are alike in the respect that each has three positions available for attack in the first stage of resin formation (two positions ortho and one position para to the hydroxyl group, the meta position being unreactive). In short each can give rise to different condensations depending upon the point of attack. On the other hand, o- and p-cresol have only two positions in their molecule free for attack. Likewise, 2,3-, 2,5- and 3,4-xlenols have two vulnerable positions. Phenols which have only a single reactive hydrogen in the benzene ring (2,4- and 2,6-xlenols) would be expected to do one of two things: either to combine with formaldehyde in equimolecular proportions or else to condense in the ratio of two molecules of phenol for each molecule of formaldehyde, to give a diphenylolmethane of the type  $\text{HOC}_6\text{H}_4\text{—CH}_2\text{—C}_6\text{H}_4\text{OH}$ . Further condensation involving aromatic hydrogens would not be expected if the positions ortho and para to the hydroxyl are blocked by alkyl groups. However, when phenol homologues having more than one reactive position are condensed with formaldehyde, not only are isomeric compounds obtained in the initial step, but alternative modes of subsequent condensation and polymerization are possible.

#### PHENOL ALCOHOLS

Reference has been made to two of the types of derivatives from phenol-formaldehyde condensation, viz., phenol alcohols and diphenylolmethanes. The former class is obtained when condensation occurs in alkaline solution, while the latter are usually isolated from an acid medium. The phenol alcohols are unstable to heat, which converts them into soluble resins.<sup>2</sup> Acetic anhydride removes the elements of water from saligenin<sup>3</sup> forming products representing various stages of dehydration. In this way a resin analyzing for carbon, 77.7, and for hydrogen, 5.8 per cent was obtained. This corresponds to the loss of 7 water molecules from 8 molecules of saligenin. The isolation of phenol alcohols from the condensation of phenol and formaldehyde was accomplished by Manasse<sup>4</sup> and Lederer.<sup>5</sup> Auwers and co-workers<sup>6</sup> found that concentrated alkali favored the formation of p-hydroxybenzyl alcohols, and that milder alkalies such as lime produced a certain amount of diphenylolmethane derivatives. The possibility of the formation of di-alcohols was also considered. Thus, Ullmann and Brittner<sup>7</sup> prepared 2,6-dimethylol-p-cresol

<sup>2</sup> R. Piria, *Ann.*, 1843, 48, 37. See Chapter 13

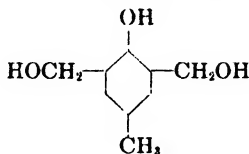
<sup>3</sup> F. Beilstein and F. Seelheim, *Ann.*, 1861, 117, 84.

<sup>4</sup> O. Manasse, *Ber.*, 1894, 27, 2409. U. S. P. 526,786, 1894.

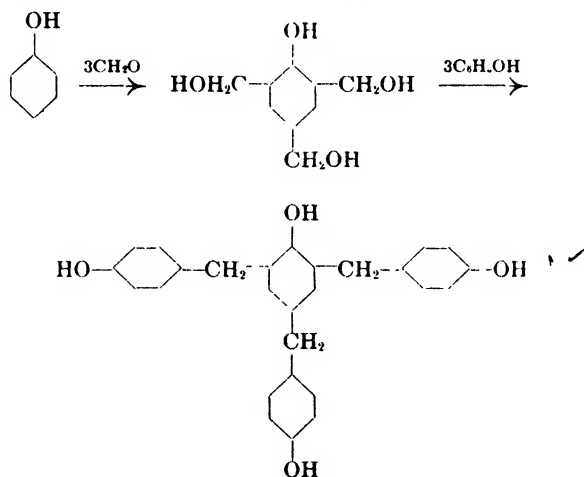
<sup>5</sup> L. Lederer, *J. prakt. Chem.*, 1894, 50 (2), 225; *J.S.C.I.*, 1895, 14, 63. U. S. P. 563,975, July 14, 1896. See *J.S.C.I.*, 1895, 14, 297.

<sup>6</sup> K. Auwers and H. van de Rovert, *Ann.*, 1898, 302, 99. K. Auwers and H. Ercklentz, *Ann.*, 1898, 302, 107. K. Auwers and O. Anselmino, *Ber.*, 1902, 35, 137. K. Auwers, *Ber.*, 1907, 40, 2524.

<sup>7</sup> F. Ullmann and K. Brittner, *Ber.*, 1909, 42, 2539.



by reacting 108 g. p-cresol dissolved in 200 cc. water containing 50 g. sodium hydroxide with 215 g. of a 35 per cent formaldehyde solution. After 4 days, the mass had become crystalline. Upon acidification of a solution of this sodium 2,6-dimethylol-p-cresylate with dilute acetic acid, a 91 per cent yield of 2,6-dimethylol-p-cresol was obtained. The recrystallized product melted at 135°C. Similar compounds from o-cresol received mention by Granger<sup>8</sup> who was able to prepare a definite di-alcohol of o-cresol and who also postulated the existence of di- and tri-alcohols of phenol and m-cresol in the syrupy products obtained from them. The xylenols form mono-alcohols with considerable ease,<sup>9</sup> but they evidently are reluctant to take up their full quota of formaldehyde molecules to form poly-alcohols. Steric hindrance may be the cause of the unreactivity which appears when the first  $-\text{CH}_2\text{OH}$  group has been introduced into a xyleneol. Amann and Fonrobert recommend the isolation of definite phenol alcohols prior to conversion into synthetic resins.<sup>10</sup> Megson<sup>11</sup> represents the formation of branched-chain resin compounds from poly-alcohols by the following scheme.



It is of interest to note that hydroxybenzyl alcohols, and resins derived from them, are formed in reactions other than phenol-formaldehyde condensations. Gsell<sup>12</sup> undertook to condense phenol and chloroform in alkaline solution in order to prepare hydroxybenzaldehydes. He found that the latter were unstable under the experimental conditions, and underwent the Cannizzaro reaction ( $2\text{RCHO} \rightarrow \text{RCOOH} + \text{RCH}_2\text{OH}$ ). The hydroxybenzyl alcohols which were formed were converted into plastic masses by the alkali. A similar experience was recorded by

<sup>8</sup> F. S. Granger, *Ind. Eng. Chem.*, 1932, 24, 442. See also German P. 474,561, 1925, to Chem. Fabr. K. Albert G. m. b. H.; *Chem. Abs.*, 1929, 23, 3114.

<sup>9</sup> E. Bamberger, *Ber.*, 1903, 36, 2036. N. J. Megson and A. A. Drummond, *J.S.C.I.*, 1930, 49, 251.

<sup>10</sup> A. Amann and E. Fonrobert, U. S. P. 1,614,172, 1927, to Chem. Fabr. K. Albert G. m. b. H.; *Brit. Chem. Abs. B*, 1927, 148. British P. 261,472, 1925; *Brit. Chem. Abs. B*, 1927, 119.

<sup>11</sup> N. J. L. Megson, *J.S.C.I.*, 1933, 52, 431T.

<sup>12</sup> J. Gsell, *Chem.-Ztg.*, 1914, 38, 541; *J.S.C.I.*, 1914, 33, 875.

Shoesmith.<sup>13</sup> He attempted to isolate the hydrolysis products of *o*-chlorotolyl carbonate  $\text{CO}(\text{OC}_6\text{H}_4\text{CH}_2\text{Cl})_2$  in acid solution. Instead of hydroxybenzyl alcohol, he obtained a resin. Pauly and Schanz,<sup>14</sup> investigating reactions which would produce substituted hydroxybenzyl alcohols, avoided resinification by using (as the condensing agent) a quantity of potassium carbonate just sufficient to produce bluing of litmus. In the case of chloral and phenol, a 60-70 per cent yield of *p*-hydroxyphenyltrichloromethylcarbinol,  $\text{HOC}_6\text{H}_4\text{CH}(\text{OH})\text{CCl}_3$ , was secured. The time required was 6 weeks.

#### DIARYLMETHANES

Preparation of compounds of the type  $\text{HOC}_6\text{H}_4\text{CHRC}_6\text{H}_4\text{OH}$  by condensing aldehydes with phenols in the presence of acids is sometimes referred to as the Baeyer reaction.<sup>15</sup> As an example of this reaction, 100 g. of acetaldehyde are mixed with 856 g. of phenol and a few drops of concentrated hydrochloric acid are added. Crystallization of the reaction product from phenol gives a substance said to be *p*-diphenylolethane plus a molecule of phenol of crystallization. When this molecule of phenol is removed by distillation, crystalline diphenylolethane is obtained (m.p. 122.9°C.). A large number of homologues of diphenylolethane have been made<sup>16</sup> in this manner.

Trautenberg<sup>17</sup> called attention to the fact that not only 4,4'-diphenylolmethane (m.p. 158°C.) and the 2,4' isomer (m.p. 115°) were isolable from the condensation of phenol and formaldehyde, but that there was also formed a certain amount of a triphenylolmethane (aurin). It has been noted<sup>18</sup> that a yellow-gray resin precipitated when equal quantities of phenol and 35 per cent formaldehyde solution were heated in a quartz flask for 50-60 hours on a water bath under reflux. The mixture was filtered. From the resin were isolated crystals of 4,4'-dihydroxydiphenylmethane, and from the filtrate, 2,4'-dihydroxydiphenylmethane. A small quantity of saligenin was also obtained from the resin.<sup>19</sup>

Substituted phenols have been observed to react with formaldehyde in acid solution to yield diphenylolmethane derivatives. Thus, *p*-nitrophenol yielded a mixture of (5,2- $\text{O}_2\text{N}(\text{HO})\text{C}_6\text{H}_3$ )<sub>2</sub>CH<sub>2</sub> and 6-nitrobenzo-1,3-dioxin.<sup>20</sup>

Although an acid medium is usually desirable for the preparation of diphenylolmethane and its homologues, certain phenolic compounds form diarylmethanes both by acid and by alkaline condensation. This is true of the naphthols.<sup>21</sup> Polyvalent phenols give not only diarylmethanes but also triarylmethanes without the use of acid catalysts.

A number of observations have been made which throw light upon the chemistry

<sup>13</sup> J. B. Shoesmith, *J.C.S.*, 1923, 123, 2699.

<sup>14</sup> H. Pauly and H. Schanz, *Ber.*, 1923, 56, 979; *Chem. Abs.*, 1923, 17, 3171.

<sup>15</sup> A. Baeyer, *Ber.*, 1872, 5, 25, 280, 1096. R. Fabinyi, *Ber.*, 1878, 11, 283. W. Städel, *Ann.*, 1878, 194, 329. T. Zincke, *Ann.*, 1898, 302, 237. A. Claus and E. Trainer, *Ber.*, 1886, 19, 3004. K. Auwers and Rietze, *Ann.*, 1907, 356, 153. A. Lunjak, *J. Russ. Phys.-Chem. Soc.*, 1904, 36, 301; 1908, 40, 466; *Chem. Zentr.*, 1904, 1, 1650; 1908, 2, 589.

<sup>16</sup> W. C. Harden and E. E. Reid, *J.A.C.S.*, 1932, 54, 4325.

<sup>17</sup> I. K. Trautenberg, *Z. angew. Chem.*, 1932, 36, 515.

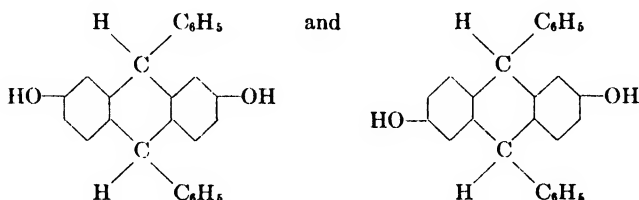
<sup>18</sup> T. Shono, K. Kizawa and T. Doha, *J. Soc. Chem. Ind. Japan*, 1931, 34, (Suppl. binding), 262; *Chem. Abs.*, 1932, 26, 261.

<sup>19</sup> See also N. N. Vorozhtsov and E. N. Yurnigina, *Zhur. Obschei. Khim., Khim. Ser.*, 1931, 1, 49; *Chem. Abs.*, 1931, 25, 4521.

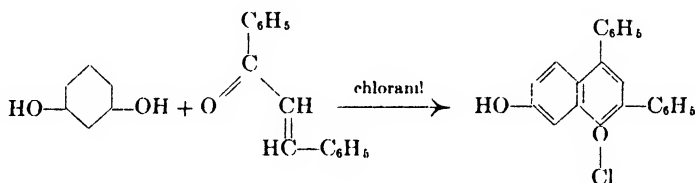
<sup>20</sup> F. D. Chattaway and R. M. Goepf, *J.C.S.*, 1933, 699. F. Calvet and E. Seijo, *Anales soc. espan. fis. quim.*, 1933, 31, 889. F. D. Chattaway and A. A. Morris, *J.C.S.*, 1927, 2018. F. Calvet and M. Carnero, *Anales soc. espan. fis. quim.*, 1932, 30, 445; *Chem. Abs.*, 1932, 26, 4605. F. Calvet and M. N. Mejuto, *Anales soc. espan. fis. quim.*, 1932, 30, 767; *Chem. Abs.*, 1932, 27, 298. F. D. Chattaway, *J.C.S.*, 1926, 2720. F. D. Chattaway and F. Calvet, *J.C.S.*, 1928, 1085. F. D. Chattaway and F. Calvet, *Anales soc. espan. fis. quim.*, 1928, 26, 417; *Chem. Abs.*, 1929, 23, 2182. F. D. Chattaway and F. Calvet, *Anales soc. espan. fis. quim.*, 1928, 26, 75; *Chem. Abs.*, 1928, 22, 1965. F. D. Chattaway and A. A. Morris, *J.C.S.*, 1928, 3241.

<sup>21</sup> E. Scheel, *Rev. gen. mat. color.*, 1929, 33, 270; *Chem. Abs.*, 1929, 23, 5320. K. Brass and P. Sommer, *Ber.*, 1928, 61, 993.

of the diphenylmethanes. Gomberg<sup>22</sup> made monohydroxydiphenylmethanes by the action of benzyl chloride on phenol in the presence of zinc dust, copper-bronze or aluminum chloride. In alkaline media, phenylbenzyl ether was produced. Huston<sup>23</sup> obtained similar results by heating a solution of benzyl alcohol and phenol in light petroleum, using aluminum chloride as a catalyst. An interesting tendency towards the formation of condensed rings is indicated by the reaction between phenol and benzaldehyde in acid media:<sup>24</sup>



Condensation of p-nitrobenzaldehyde with 2 molecules of  $\beta$ -naphthol gave ms-[4-nitrophenyl]-dinaphthopyran.<sup>25</sup> Formaldehyde combined with 2 molecules of  $\beta$ -naphthol in the presence of a trace of hydrochloric acid, yielding dinaphthopyran.<sup>26</sup> The initial product from furfural and phenol in acid solution is  $\text{C}_6\text{H}_5\text{OCH}(\text{OH})\text{C}_6\text{H}_5\text{OH}$ .<sup>27</sup> Robinson and Walker<sup>28</sup> obtained benzopyrylium salts by condensing a reactive phenol with an unsaturated aldehyde or ketone in acid solution and in the presence of an oxidizing agent. Good yields of 7-hydroxy-2,4-diphenylbenzopyrylium chloride were obtained from resorcinol and benzylideneacetophenone with chloranil:



#### THEORIES OF CONSTITUTION OF PHENOL-FORMALDEHYDE PRODUCTS

Baekeland<sup>29</sup> viewed the phenol-formaldehyde reaction as a condensation and polymerization which took place in three stages, the resinous materials formed being termed respectively *initial condensation product A*, *intermediate condensation product B* and *final condensation product C*. These designations have now come into universal use. Under ordinary conditions, A may be liquid, pasty or solid. B is an insoluble solid which swells upon addition of acetone, phenol or terpeneol. B can be melted (or, rather, softened by heat) a limited number of times before

<sup>22</sup> M. Gomberg, *J. A. C. S.*, 1920, 42, 2039.

<sup>23</sup> R. C. Huston, *J. A. C. S.*, 1924, 46, 2775.

<sup>24</sup> O. Hinsberg, *Ber.*, 1929, 62, 418. See also I. Tanasescu and T. Simonescu, *J. prakt. Chem.*, 1934, 141, 311-326.

<sup>25</sup> O. Dischendorfer and E. Nesitka, *Monatsh.*, 1928, 50, 16; *Chem. Abs.*, 1928, 22, 3656. O Dischendorfer, *Monatsh.*, 1928, 49, 133.

<sup>26</sup> W. Kuster and E. Schoder, *Z. physiol. Chem.*, 1927, 170, 44; *Brit. Chem. Abs.*, A, 1928, 48.

<sup>27</sup> A. E. Forst-Koshits, N. Kudryavtsev and B. Mashkileison, *Kunststoffe*, 1933, 23, 97; *Chem. Abs.*, 1933, 27, 3709.

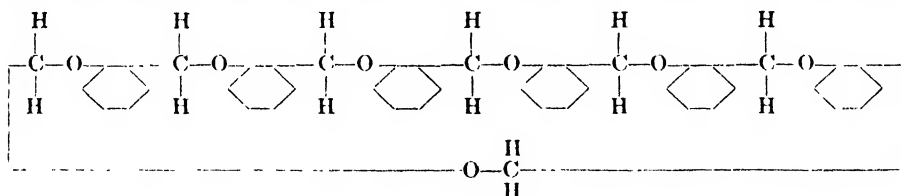
<sup>28</sup> R. Robinson and J. Walker, *J. C. S.*, 1934, 1435.

<sup>29</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1909, 1, 149.

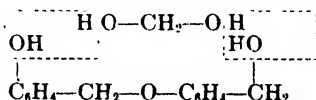
it is converted into C, which is infusible and indifferent to all solvents. The nature of these materials renders it excessively difficult to obtain experimental evidence concerning their structures. The problem of purification increases with the complexity of the substances, until, in the case of Bakelite C, we have a material which can neither be dissolved, distilled nor melted. The determination of molecular weight, for instance, is not a simple matter.

In the study reported in 1909, Baekeland<sup>30</sup> compared the products of three different reactions: (1) saligenin plus phenol (2) phenol plus formaldehyde with an alkaline catalyst and (3) phenol plus formaldehyde with an acid catalyst. Saligenin reacted with phenol to give a soluble fusible resin identical with the material made by acid condensation. However, a reaction corresponding to an alkaline condensation of phenol with formaldehyde gave a different product. Thus saligenin was heated with varying amounts of formaldehyde and it was found that at least one-sixth of a molecular proportion of the latter was necessary to produce stage C. With smaller amounts of formaldehyde the product was always one which was attacked by solvents. Using sealed tubes and a small amount of base as catalyst, elimination of a certain amount of water marked stage A. Elimination of more water resulted in stage B, but the transformation of the latter into stage C involved no further splitting of water and no change in volume, suggesting polymerization as the probable explanation of the change from B to C.

Baekeland made certain tentative explanations of these phenomena. Assuming that saligenin condensed with itself through the intermolecular reaction of phenolic and aliphatic hydroxyl groups, and in view of the fact that one-sixth of a molecular proportion of formaldehyde must be added to convert saligenin into the final resin, stage C was considered to be made up of units such as the following:



An advantage possessed by this type of structure is that it leaves open the possibility of varying the number of saligenin units to be condensed with a single molecule of formaldehyde. Thus, Lebach<sup>31</sup> obtained a substance formulated as



The intermediate products which Baekeland prepared by acid condensation were more amenable to inspection than those obtained through the use of alkali. It was noted that when 15 mols of phenol were heated with 14 mols of formaldehyde in the presence of a small amount of hydrochloric acid a soluble fusible variety of resinous mass (Novolak) was obtained. In acid solutions, an excess of phenol over that indicated in the proportions above quoted was beneficial to the formation of Novolaks. On the other hand, even when an excess of phenol was employed, alkaline condensations did not produce the Novolak variety of resin, but infusible insoluble products. Whenever an excess of phenol was used, either in

<sup>30</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1909, 1, 158.

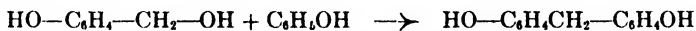
<sup>31</sup> H. Lebach, *Z. angew. Chem.*, 1909, 22, 1599.



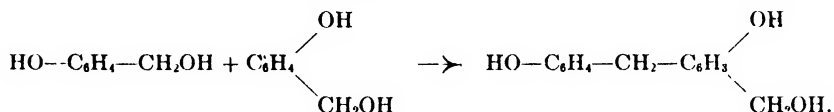
acid or alkaline solution, free phenol was present in the final product. Analysis of the resin from acid condensation verified its identity with that obtained by heating saligenin with phenol. Each of the resins had the constitution  $C_{20}H_{28}O_4$ .

In contradistinction to Baekeland's "ether-linkage formation" hypothesis, Raschig<sup>22</sup> suggested that the phenol alcohols which are formed initially may react in two ways:—

- (1) with more phenol to give diphenylolmethanes

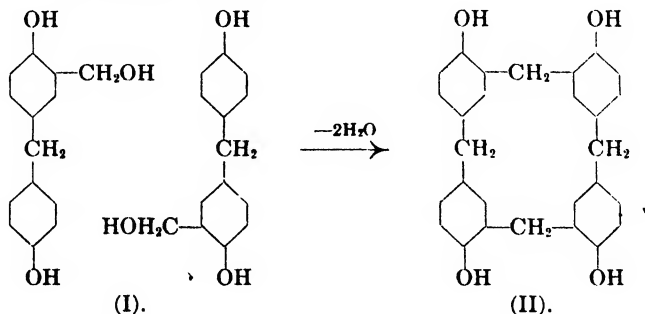


- (2) with themselves to form alcohols of diphenylolmethanes



When the reactants in equation (1) are phenol or o- or p-hydroxybenzyl alcohol, three isomeric dihydroxydiphenylmethanes should be produced. As noted earlier in this chapter, two of these isomers, 2,4'- and 4,4'-dihydroxydiphenylmethane, have been isolated by various workers from actual resin preparations. The 2,2'- derivative has been crystallized only in the form of an ether or ester. Raschig stated that soluble fusible resins arise when less than one molecular proportion of formaldehyde per molecule of phenol is used, while the insoluble products are formed when the formaldehyde is in excess of this amount usually to the extent of about 10-20 per cent. In the former case the relative molecular proportions would favor the production of diphenylolmethanes. If saligenins were formed these would condense with the excess of phenol to give the diarylmethane. Baekeland has shown<sup>23</sup> that diphenylolmethanes are converted into insoluble infusible resins by heating with paraformaldehyde. In the latter case, i.e., when formaldehyde exceeds one molecular equivalent, Raschig postulated that the resins are mixtures of great complexity, the products of the earlier stages of their formation being diarylmethanes and phenol alcohols. These two classes of compounds can condense with one another as well as with more phenol. The ultimate material would consist not only of molecules of great size, but of molecules of various sizes, e.g.,

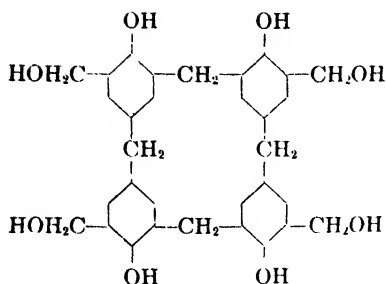
A. Two molecules of the mono-alcohols of diphenylolmethane combine with loss of two molecular proportions of water.



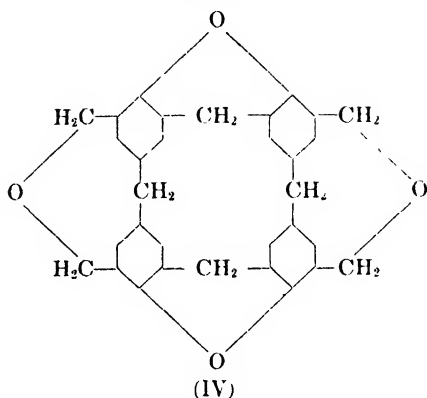
B. With double the proportion of formaldehyde and assuming that a di-alcohol of phenylolmethane is present as one stage in the reaction, the product becomes (III).

<sup>22</sup> F. Raschig, *Z. angew. Chem.*, 1912, 25, 1945; *Chem. Abs.*, 1913, 7, 887.

<sup>23</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1913, 5, 507.



(III).



(IV)

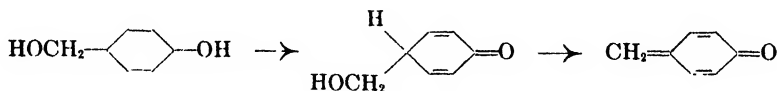
C. This may condense further with the elimination of water to give Raschig's representation of Bakelite (IV).

Formulas II, III and IV are obviously only some of the many that can be conceived possible by similar reactions. After the publication of Raschig's work and views, Baekeland suggested the possibility that the resins may be composed of material which is still more complex than the compounds described by Raschig, and that, if the latter bodies were present, "together with an endless variety of other chemical individuals," their relative importance was not understood. Redman, Weith and Brock<sup>84</sup> state that Raschig's formulations are not in agreement with actual analyses.

Raschig also demonstrated that the action of heat alone on either o- or p-saligenin could produce saliretins but with a mixture of the two, and a basic catalyst, an insoluble infusible material was formed. He concluded from this evidence that both saligenins were necessary to produce Bakelite types of resin. Baekeland<sup>85</sup> investigated this point still further as it was contrary to the views he had expressed in his first paper. He found that if maintained at 160°C. for about 6 hours, o- and p-saligenins alone or in admixture with either ammonia or caustic soda as catalyst did not produce insoluble and infusible resins but only brittle infusible bodies which were immediately soluble in caustic soda. However, with an added amount of paraform (as little as 5 per cent) the product was of great hardness and was unattacked by caustic soda.

Neither Raschig nor Baekeland at that time undertook to assign any definite reason for the polymerization to a hard insoluble body. It is inconceivable that the resin would become insoluble simply on account of the complexity of its component molecules. Moreover molecular size alone is no criterion of insolubility (*cf.* starch and protein).

Wohl and Mylo<sup>86</sup> reasoned that p-saligenin by changing to its tautomeric form would lose water and thus furnish a quinoid compound which will then polymerize under the experimental conditions employed.

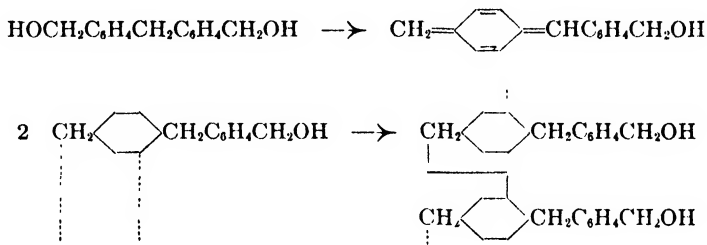


<sup>84</sup> L. V. Redman, A. J. Weith and F. P. Brock, *Ind. Eng. Chem.*, 1914, 6, 3.

<sup>85</sup> L. H. Baekeland, *loc. cit.*

<sup>86</sup> A. Wohl and B. Mylo, *Ber.*, 1912, 45, 2046

A similar reasoning would apply to o-saligenin. Only a small amount of evidence or support for these views has since been put forward. Sugimoto<sup>27</sup> states that Bakelite has an empirical formula  $C_7H_6O$  agreeing with that of the quinoid compound mentioned above. A similar view was supported by Connerade,<sup>28</sup> who condensed benzyl chloride with trioxymethylene in acetic acid at 50°C. using sulphuric acid as the catalyst. He obtained the 2,4'- and 2,2'-dichloromethyl-diphenylmethanes which were converted into the corresponding iodo compounds. Treatment of the latter with silver nitrate to replace the iodine by a nitrate group was accompanied by polymerization. Hence subsequent hydrolysis gave rise to a polymer of the di-alcohol of diphenylmethane. Connerade's formulation of the reaction requires the presence of quinoid forms:



Driver<sup>29</sup> states that the resin formed during the preparation of hydroxy-benzaldehydes by the Reimer-Tiemann synthesis,<sup>30</sup> is not due to condensation of the aldehydes with phenols in alkaline media. In acid media, however, they do combine with phenol in equimolecular proportions to give complex alkali-soluble red resins of empirical formula  $C_{13}H_{10}O_2$ . The resins are assumed to be polymers of the quinoid anhydride of 2,4'-dihydroxybenzhydrol.

In order to determine the kinetics of the reaction, Jablonower<sup>31</sup> studied the increase in density when phenol and formaldehyde reacted in the presence of ammonia. His results supported Baekeland in that the initial stage was shown to be one of condensation, followed by polymerization.

Van Voorhout<sup>32</sup> investigated the effects of varying the catalyst. He identified o- and p-saligenin as intermediate products under alkaline conditions. In acid media 4,4'-diphenylolmethane was formed. His results indicated that the stronger the base the stronger its condensing power. Bakelite was postulated as mainly polymerized diphenylolmethane associated with traces of unchanged material in solid solution.

Beatty<sup>33</sup> condensed diphenylolpropane with aqueous formaldehyde under alkaline conditions and suggested that the reaction proceeded as follows:—the first stage as in equation (1) to form an alcohol while further condensation occurs as in equation (2) with the elimination of water.

<sup>27</sup> S. Sugimoto, *Reports Osaka Ind. Research Inst. Japan*, 1929, 10, 10; 1927, 8, 7; 1928, 9, 2; *Chem. Abs.*, 1930, 24, 837; 1928, 22, 142; 1929, 23, 2762.

<sup>28</sup> E. Connerade, *Bull. soc. chim. Belg.*, 1932, 41, 337, *Brit. Chem. Abs. A*, 1932, 1122.

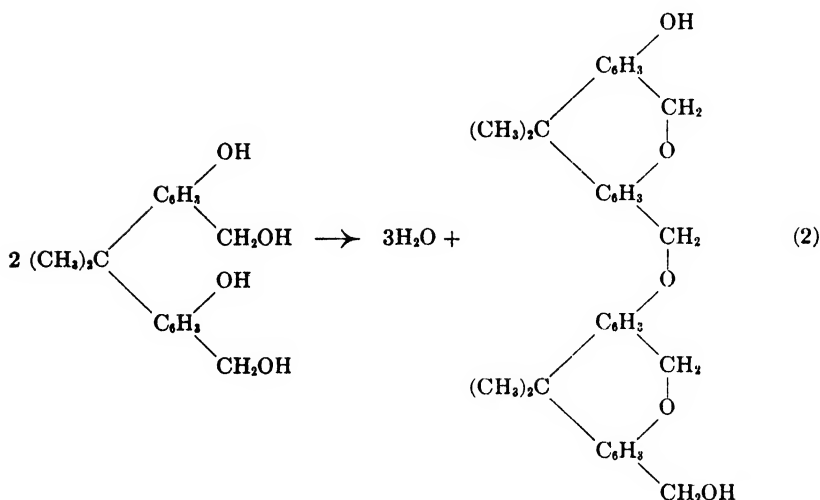
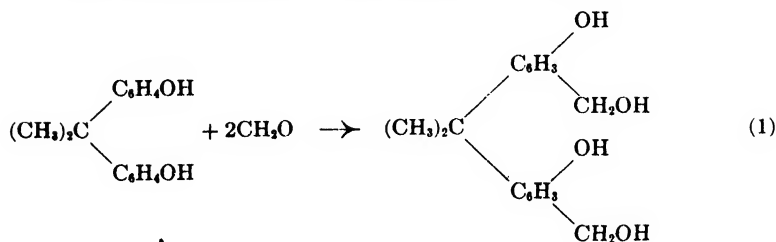
<sup>29</sup> J. E. Driver, *J. S. C. I.*, 1927, 46, 197T.

<sup>30</sup> The production of hydroxylaldehydes by the action of chloroform on alkaline phenols (K. Reimer, *Ber.*, 1876, 9, 423; *J. C. S.*, 1876, 30 (2), 82. K. Reimer and F. Tiemann, *Ber.*, 1876, 9, 824; *J. C. S.*, 1876, 30 (2), 632).

<sup>31</sup> B. Jablonower, *J. A. C. S.*, 1913, 35, 811.

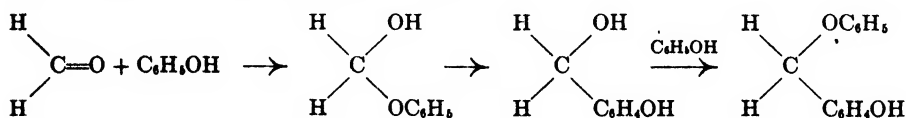
<sup>32</sup> A. W. C. van Voorhout, *Chem. Weekblad*, 1920, 17, 2; *Kunststoffe*, 1921, 11, 59.

<sup>33</sup> W. A. Beatty, *U. S. P.* 1,225,748, May 15, 1917; *Chem. Abs.*, 1917, 11, 2142. See Chapter 18.



Herzog and Kreidl,<sup>44</sup> emphasizing the fact that unsaturation was a marked feature of compounds which are known to polymerize, suggested the presence of the grouping  $-\text{CO}-\text{CH}=\text{CH}-$  in Bakelite A and B to account for their properties. A quinonoid rearrangement of Raschig's formulas was written so as to include this grouping.

In 1925 Baekeland and Bender<sup>45</sup> reviewed previous work and recorded some experimental data in support of a new hypothesis in which the role of ethers was still an important one. When hydrochloric acid was employed as the catalyst they distinguished three chemical steps in the condensation of formaldehyde and phenol. (1) Two molecular proportions of phenol combine with one of formaldehyde to give an unsymmetrical ether, p-hydroxyphenylphenoxymethane, which they regard as being the chief constituent of the fusible soluble resin. The steps in the formation of this ether may be represented by:

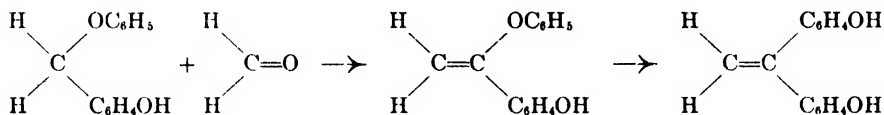


Further rearrangement of the ether yields dihydroxydiphenylmethane (diphenylol-

<sup>44</sup> W. Herzog and J. Kreidl, *Z. angew. Chem.*, 1922, 35, 641; *Chem. Abs.*, 1923, 17, 1722.

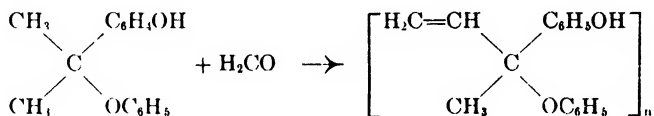
<sup>45</sup> L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, 1925, 17, 225. A survey of views on the constitution of phenol resins is given by H. Tatu, *Rev. gén. mat. plast.*, 1934, 10, 449; *Brit. Chem. Abs. B*, 1935, 319; *Chem. Abs.*, 1935, 29, 3068.

methane). (2) Condensation of the ether with another molecule of formaldehyde, union occurring at the methylene group. This gives rise to Stage B.

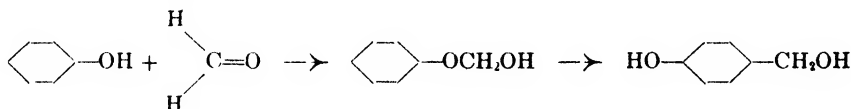


(3) Polymerization of the unsaturated compounds obtained in the second step is believed to mark a gradual passage to Stage C.

When acetaldehyde or acetone replaces formaldehyde, the  $\text{CH}_2$  grouping of the product obtained in the first step then becomes  $\text{CH}_3\text{CH}$  or  $(\text{CH}_3)_2\text{C}$ , respectively. Such fusible soluble resins can combine further<sup>46</sup> with formaldehyde to reach Stage C. The possible reaction for the derivative from acetone, for example, is:



Alkaline condensation of formaldehyde with phenol is postulated as taking place through an intermediary ether which subsequently rearranges to p-saligenin.



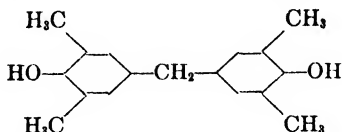
Baekeland and Bender treated phenol with n-butyraldehyde (in the presence of dry hydrogen chloride) with the expectation that the speed of reaction would be sufficiently slow to enable them to isolate large yields of the intermediaries, thereby obtaining convincing evidence that ether formation was involved in the preparation of phenolic resins. After seven days the mass had become a jelly with much crystalline material in suspension. On separation the latter was proved to be  $\alpha,\alpha,\text{p},\text{p}'$ -dihydroxydiphenylbutane (m.p.  $136^\circ\text{C}.$ ) (yield 38 per cent). The resinous residue was found to have the same empirical formula, and similar molecular weight, but only one free hydroxyl group could be detected by titration. When the resin was heated at  $260\text{--}310^\circ\text{C}.$  under reduced pressure (22 mm.) 79 per cent distilled over. This distillate solidified and proved to be identical with the crystalline material melting at  $136^\circ\text{C}.$  It was considered that the resin was phenoxy-p-hydroxyphenylbutane and that heating rearranged it to the diarylbutane.<sup>47</sup>

Baekeland and Bender's views are such as to suggest that any phenol will condense with formaldehyde to a resin so long as it can yield first a diphenylol-methane. The highly polymerizable substance is formed by combination of formaldehyde with the methylene grouping joining the two nuclei. It has been shown<sup>48</sup> that 2,6-dimethylphenol (a "single-position" phenol) will yield a Novolak resin, though a considerable amount of hydrochloric acid as catalyst is necessary. The dioxynolmethane formed must have the structure,

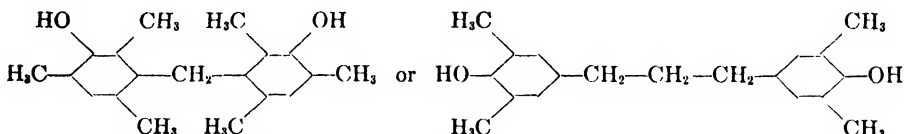
<sup>46</sup> Cf. J. Scheiber and K. Sändig, "Artificial Resins," English Translation by E. Fyleman, Isaac Pitman & Sons, Ltd.; London, 1931, 97.

<sup>47</sup> Similar rearrangements have often been observed. See M. Gomberg and R. L. Jickling, *J.A.C.S.*, 1915, 37, 2575. J. B. Niederl and E. A. Storch, *J.A.C.S.*, 1933, 55, 284. R. A. Smith, *J.A.C.S.*, 1934, 56, 717.

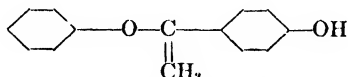
<sup>48</sup> F. S. Granger, *Ind. Eng. Chem.*, 1932, 24, 446.



No further reaction with formaldehyde occurs, the reason assigned being that no active position remains open to substitution.<sup>49</sup> Mesitol<sup>50</sup> (2,4,6-trimethylphenol) reacts with formaldehyde to give a crystalline substance (m.p. 186-187°C.) formulated as:

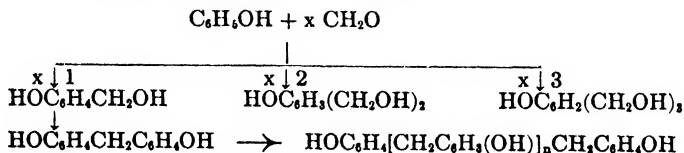


According to Megson, the dixylenolmethanes are converted gradually into resins, and he therefore believes dihydroxyarylmethanes to be true resin intermediates. Megson objected to Baekeland and Bender's idea that resinoid C is a polymer of the ether type



on the grounds that rate of resinification (conversion to resinoid C) is so largely governed by the nature and positions of the substituents in the phenyl groups. He therefore subscribed to the theory that polyalcohols and branched-chain structures were involved.

The idea that di- and tri-alcohols may be formed was stressed by Amann and Fonrobert<sup>51</sup> who suggested the following scheme:



Thus, the resin was thought to consist of a long chain of hydroxybenzyl groups.

Blumfeldt<sup>52</sup> proposed that an "idealized" formula for Bakelite C be given by the structure (b) shown on next page. Such a representation could result from the condensation of two long molecules of the type (a). (For a further discussion of this work in relation to the structure of resins in general, see Chapter 4.) This would indicate a hydrocarbon of very compact structure and low hydrogen content, somewhat similar to what has been postulated for graphite,<sup>53</sup> but while the latter is of course insoluble it has marked crystalline features with a cleavage plane, a factor influencing its use as a lubricant. No such property has been discovered in Bakelite C. Analytical results do not agree with such a small oxygen content.

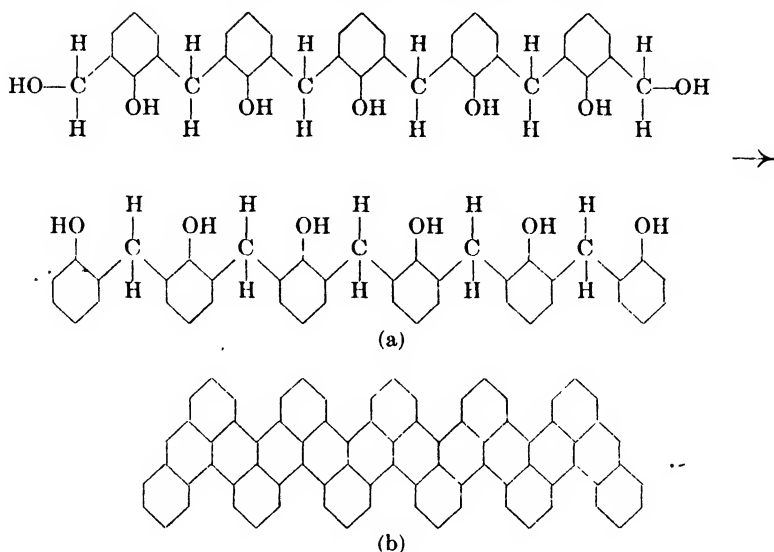
<sup>49</sup> Carbon atoms which are ortho or para to the phenolic group and to which no substituting groups are attached are designated active positions.

<sup>50</sup> N. J. L. Megson, *J.S.C.I.*, 1933, 52, 421T.

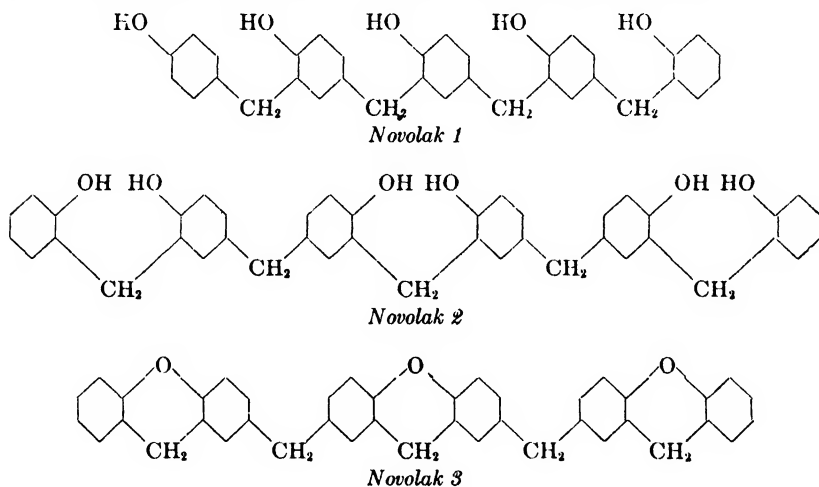
<sup>51</sup> A. Amann and E. Fonrobert, British P. 261,472, 1925, to Chem. Fabr. K. Albert G. m. b. H.; *Brit. Chem. Abs.* B, 1927, 119.

<sup>52</sup> A. E. Blumfeldt, *Chem.-Ztg.*, 1929, 53, 493; 1931, 55, 551; *Chem. Abs.*, 1929, 23, 5179; 1932, 26, 609.

<sup>53</sup> L. Wallerstein (U. S. P. 1,442,372, Jan. 16, 1923; *Chem. Abs.*, 1923, 17, 1115) has found that the carbon derived from charred phenol-formaldehyde resin is highly absorptive, and is comparable with coals produced by the carbonization of animal or vegetable matter.



It is to be noted that Blumfeldt utilized only ortho-substituted rings in this case and he did this specifically for he regarded the Novolaks as being, in their idealized form, chains made up in a manner requiring para substitution.



According to Blumfeldt, these ideas explain the following four points concerning stage C:

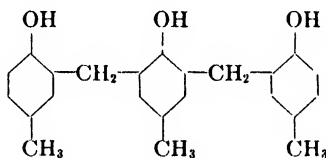
- (1) Its remarkable stability at 300°C.
- (2) When dry distilled the elements of water are not lost.
- (3) Its polymerization is exothermic.
- (4) It is very slowly attacked by alkali.

Koebner<sup>54</sup> criticized this formula on the grounds that it does not permit of a

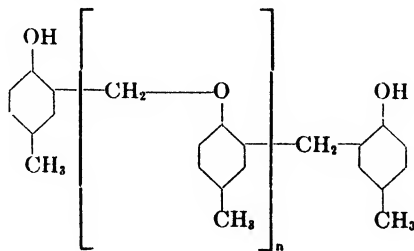
<sup>54</sup> M. Koebner, *Chem.-Ztg.*, 1930, 54, 619; *Brit. Plastics*, 1930, 2, 197; *Plastics and Molded Products*, 1930, 6, 653; *Chem. Abs.*, 1930, 24, 8039.

sufficient number of hydroxyl groups in the material to accord with the formation of sodium salts soluble in alcoholic soda, which are however insoluble in water. Its formation also necessitates the elimination of more water than actually occurs during the reaction. He regards the combination of phenol with formaldehyde as being more complex than that of the cresols and places the latter in the order of complexity of their condensations as *m*- < *o*- < *p*-. This is rather unexpected, as *m*-cresol belongs to the three-position phenols and in *p*-cresol the two substituting free positions are symmetrically placed. One would therefore expect the order to be:—condensation of *m*- much more complex than that of *o*- which is more than that of *p*-cresol. Koebner<sup>55</sup> recognized the importance of the formation of homologues and isomers of the resin intermediates. He demonstrated that 2 mols of *p*-cresol united with 1 mol of formaldehyde at 150°C. without a catalyst to form a Novolak, and that the yield of isolable dicresylmethane derivative was fairly good. However, in an experiment in which formaldehyde was condensed with phenol instead of *p*-cresol, the presence of isomers was bothersome and the yield of the diphenylmethane was small. Koebner favored the view that Novolaks are long chain molecules of the type  $R(CH_2R)_nCH_2R$ . The true Novolak would be a mixture of compounds with different values of *n*.

Koebner also showed that, accompanying the formation of a dicresylmethane from *p*-cresol and formaldehyde, there was produced a smaller amount of a crystal line substance (m.p. 215°C.) for which the analysis indicated the structure:



This three-ring compound was also made by condensing *p*-cresol-dialcohol (2,6-dimethylol-4-methylphenol) with *p*-cresol in acid solution. Hence its structure was ascertained. Koebner also prepared and isolated the compounds containing 4, 5, 6 and 7 substituted benzyl groups in a chain.<sup>56</sup> An independent isolation of the three-ring compound (m.p. 214°C.) was described by Morgan, Megson and Drummond.<sup>57</sup> Megson<sup>58</sup> reported that along with the two-ring and three-ring compounds a series of amorphous substances can be made from *p*-cresol and formaldehyde. For these he suggested the representation,



<sup>55</sup> M. Koebner, *Z. angew. Chem.*, 1933, 46, 251; *Chem. Abs.*, 1933, 27, 3783.

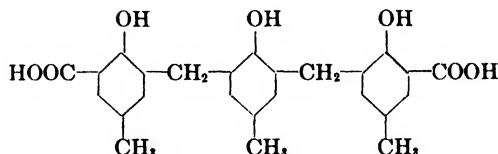
<sup>56</sup> For a discussion of the polymers formed by the action of aluminum chloride on benzyl chloride see Chapter 56.

<sup>57</sup> G. T. Morgan, N. J. L. Megson and A. A. Drummond, *J.S.C.I.*, 1930, 49, 245T, 250T. See also A. Vansheidt, A. Itenberg, P. Erlukova and G. Simonov, *Plasticheskie Massui*, 1934, 3, 17, *Chem. Abs.*, 1934, 28, 6578. A. Vansheidt, *Plasticheskie Massui*, 1934, 2, 1; *Chem. Abs.*, 1934, 28, 6326.

<sup>58</sup> N. J. L. Megson, *J.S.C.I.*, 1930, 49, 249T.

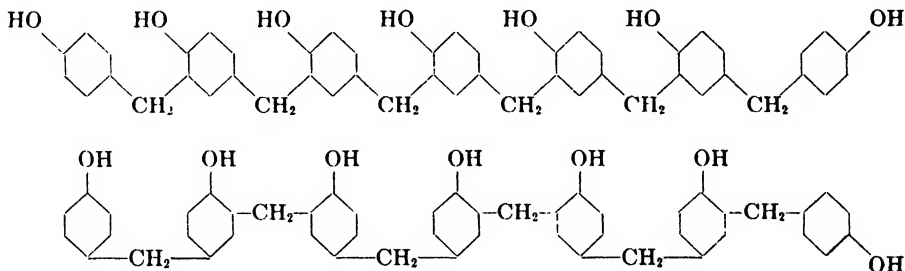


An acid of the formula



has been prepared<sup>80</sup> by condensing p-cresoldialcohol with 2 mols of p-cresolcarboxylic acid in the presence of concentrated hydrochloric acid.

Pollak and Riesenfeld<sup>80</sup> subscribed to the theory that Novolaks consist of a chain of seven phenol molecules condensed by six formaldehyde molecules when six molecules of water are eliminated. Two phenol molecules are removed when the product is treated with water or caustic soda, consequently they rejected any ring formulations for a Novolak, and suggested<sup>81</sup>



The exact configuration was not determined, and the resinous character was attributed to the presence of isomeric compounds. It was assumed that the resin was made up entirely of substances of the same molecular weight. The molecular weight determinations indicated a value of about 523 for the Novolaks, whereas a value of 730 is demanded by the theory of seven molecules of phenol combining with six of formaldehyde. The use of the Grignard reagent in pyridine solution (Zerewitinoff Method) gave evidence of the presence of 13 hydroxyl groupings per molecule as measured by the volume of methane evolved.

Hugel and Vincent<sup>82</sup> made a series of phenol-formaldehyde condensations in which they varied the concentration of both formaldehyde and catalyst. From these experiments they could detect no essential difference between acid and alkaline catalyzed products but concluded that hardening was due to the addition of an excess of formaldehyde above that required for the fusible resins. Koebner<sup>83</sup> also determined the molecular weights<sup>84</sup> of a series of Novolaks formed by acidic condensations in which the proportions of formaldehyde varied from 1 to 7 mols per 10 mols of p-cresol and found that the values so obtained increased progressively with the amount of formaldehyde used.

<sup>80</sup> British P. 374,735, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 1056.

<sup>81</sup> F. Pollak and F. Riesenfeld, *Z. angew. Chem.*, 1930, 43, 1129; *Brit. Plastics*, 1931, 3, 225; *Chem. Abs.*, 1931, 25, 1398.

<sup>82</sup> Cf. A. Amann and E. Fonrobert's formula, already discussed.

<sup>83</sup> G. Hugel and M. Vincent, *Chimie et Industrie*, 1929, (Feb. Special No.), 540; *Chem. Abs.*, 1929, 23, 4088.

<sup>84</sup> M. Koebner, *Z. angew. Chem.*, 1933, 46, 251; *Chem. Abs.*, 1933, 27, 3788.

<sup>85</sup> For a discussion of the molecular weights of the resins see G. Dring, *J.S.C.I.*, 1934, 53, 422T. See also Chapter 4.

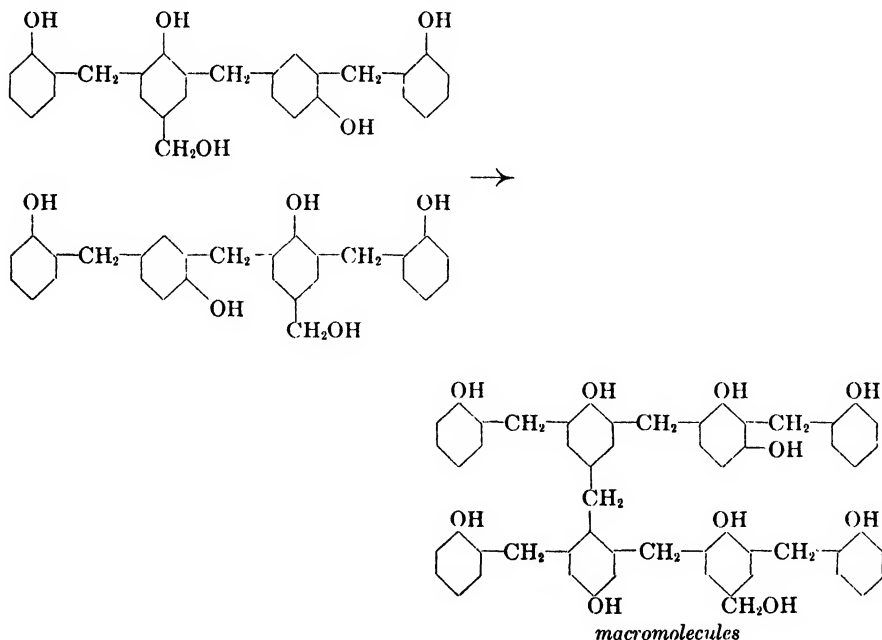
TABLE 26.—Condensations of Formaldehyde with 10 Mols. *p*-Cresol.

Gram-mol. CH <sub>2</sub> O	Yield of Resin		Mol. Wt. Found
	Found g.	Calcd. g.	
1 . . . . .	180	250	229
2 . . . . .	335	306	256
3 . . . . .	470	412	291
4 . . . . .	590	518	334
5 . . . . .	710	624	371
6 . . . . .	810	730	437
7 . . . . .	870	836	638

This is fairly conclusive evidence that, using *p*-cresol, Novolaks consist of chains of varying lengths, and of alternate cresol and methylene linkages.

If the Novolaks do consist of chains of substituted benzyl groups, the question arises as to which isomers are most likely to be involved. Megson and Drummond<sup>65</sup> quote evidence that 2,4'-dihydroxydiphenylmethane is the resin-forming intermediate. When phenol and formaldehyde condense in the presence of hydrochloric acid, both 2,4'- and 4,4'-dihydroxydiphenylmethane are obtained. Heating the mixture causes formation of resin and decrease in the quantity of 2,4'-isomer. This view is in agreement with the observation of Driver (already mentioned) that 2,4'-dihydroxybenzhydrol readily yields a resin.<sup>66</sup>

Morgan and Megson<sup>67</sup> propound further that any polynuclear compound from phenol and formaldehyde possesses free positions in internal rings at which condensation to form macromolecular structures is possible.



From this point of view, Novolaks may be regarded as substances of the general formula  $\text{HOR}''(\text{CH}_2\text{R}'''\text{OH})_x\text{CH}_2\text{R}'''\text{OH}$ . The resols, or initial products of alkaline

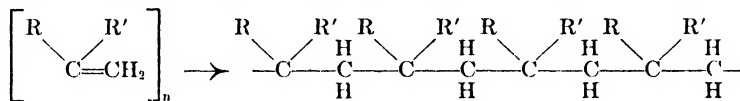
<sup>65</sup> N. J. L. Megson and A. A. Drummond, *J.S.C.I.*, 1930, 49, 251T.

<sup>66</sup> J. E. Driver, *J.S.C.I.*, 1927, 46, 197T.

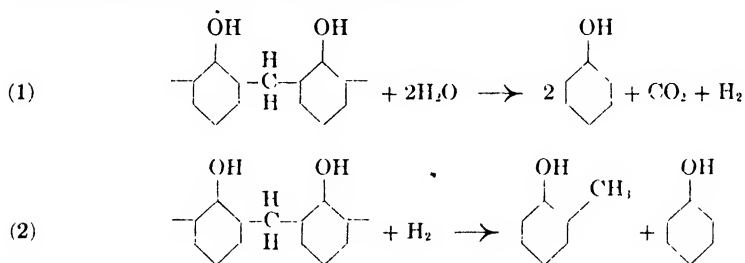
<sup>67</sup> G. T. Morgan and N. J. L. Megson, *J.S.C.I.*, 1933, 52, 420T.

condensation are mono- or poly-alcohols. Resitols (B stage resins) are macromolecules which are only partly united by methylene groups. Resites (C stage) are branched-chain macromolecules.

This theory is, of course, very much at variance with the view expressed by Baekeland and Bender (*vide supra*). A more recent version<sup>66</sup> of Baekeland's idea indicates the manner by which final polymerization might take place.



The same investigators heated phenol-formaldehyde resin in an autoclave with 10 or 15 per cent sodium hydroxide solution at 300°C. for several hours. Such hydrolyses gave higher phenols than those which were used as starting materials. It was found also that a considerable amount of hydrogen was evolved. The net result could be indicated in the following manner:



Degradation experiments evidently give interesting results, but have not yet solved the problem of resin constitution. Moehle<sup>67</sup> found that the hydrogenation of phenol-aldehyde resins at 440°C and 125 atmospheres yielded phenols and light oils.

#### PHENOL-HEXAMETHYLENETETRAMINE CONDENSATIONS

The replacement of formaldehyde by other aldehydes (or even by ketones) in the preparation of resins has no very drastic effect upon the nature of the intermediates or of the resin. The differences which do manifest themselves are such as can be easily explained, or possibly anticipated, from considerations of the properties of the particular aldehydic reactant used. When hexamethylenetetramine (hexamine) however is employed the difference is more marked.

Various workers<sup>70</sup> noted the formation of hexamethylenetetramine from ammonia and formaldehyde. Lösekann<sup>71</sup> has suggested  $\text{N}(\text{CH}_2\text{---N=CH}_2)_3$  as its constitution. Duden and Scharff<sup>72</sup> expressed the view that ammonia and formaldehyde (or its polymer), interacting with liberation of heat, yield as the first stage a product formulated as (I) the complete reaction resulting in hexamine (III) possibly through the intermediate stage (II), viz:—

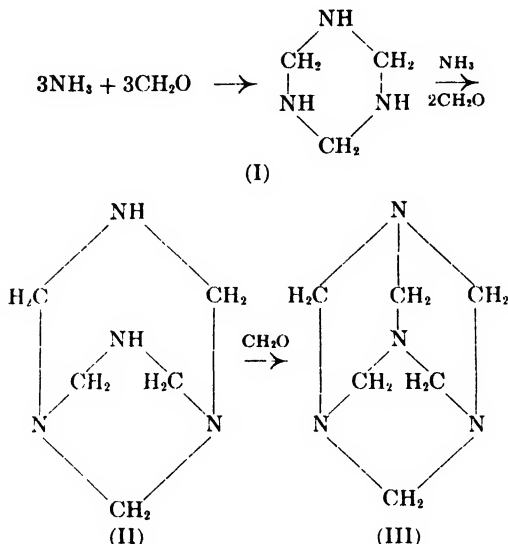
<sup>66</sup> I. Allen, V. E. Meharg and J. H. Schmidt, *Ind. Eng. Chem.*, 1934, 26, 634

<sup>67</sup> E. Moehle, German P. 370,270, 1931, to A.-G. für Steinkohleverflüssigung und Steinkohleveredelung; *Chem. Abs.*, 1933, 27, 2592.

<sup>70</sup> A. Butlerov, *Ann.*, 1860, 115, 322. A. Wohl, *Ber.*, 1886, 19, 1842. B. Tollens, *Ber.*, 1884, 17, 653. R. Cambier and A. Borchet *Compt. rend.*, 1895, 120, 557; *J. C. S.*, 1895, 68, 262.

<sup>71</sup> G. Lösekann, *Chem.-Ztg.*, 1890, 14, 1409; *J. C. S.*, 1892, 62, 423.

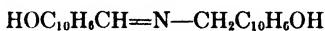
<sup>72</sup> P. Duden and M. Scharff, *Ann.*, 1895, 288, 218, 938.



This representation of hexamethylenetetramine is commonly but not universally accepted. X-Ray considerations tend, however, to support this acceptance.<sup>73</sup>

When ammonia is used as the catalyst in phenolic condensations it is assumed that hexamine is first formed. In such cases, the ammonia can be recovered almost quantitatively during dehydration of the resin product. The efficacy of hexamine in speeding up the initial condensation was found by Holmes and Megson<sup>74</sup> to be practically equal to that of ammonia in m-cresol-formaldehyde reactions. The possibility of employing hexamine in the production of phenolic resins early attracted attention<sup>75</sup> (see also Chapters 13, 15 and 16). The value of introducing dry hexamethylenetetramine as a hardening agent (rather than mixtures which would form the substance) was recognized by Aylsworth.<sup>76</sup>

Under mild conditions three molecular proportions of phenol combine with one of hexamine to form a definite compound.<sup>77</sup> A crystalline substance of composition  $\text{C}_6\text{H}_{12}\text{N}_4 \cdot \text{C}_6\text{H}_6\text{O}$  (m.p.  $176^\circ\text{C}.$ ) has also been isolated.<sup>78</sup> Harvey and Baekeland used various homologues of phenol and found that less than three molecules would combine with one of hexamine giving compounds with ill-defined melting points and strong resin-forming tendencies.  $\beta$ -Naphthol, heated with hexamethylenetetramine in acetic acid, yielded 2,2'-dihydroxy-1-naphthylidene-1'-naphthylmethylamine,



$\alpha$ -Naphthol, under similar conditions gave sym-di- $\alpha$ -naphthoxy-dimethylamine. With p-nitrophenol, hexamethylenetetramine formed an addition compound,



<sup>73</sup> R. G. Dickinson and A. L. Raymond, *J.A.C.S.*, 1923, 45, 22. H. Mark, *Ber.*, 1924, 57, 1820; *Chem. Abs.*, 1925, 19, 754.

<sup>74</sup> E. L. Holmes and N. J. L. Megson, *J.S.C.I.*, 1933, 52, 415.

<sup>75</sup> British P. 28,009, 1907, to Knoll & Co.; *J.S.C.I.*, 1908, 27, 908.

<sup>76</sup> J. W. Aylsworth, U. S. P. 1,102,594, Mar. 19, 1912; *Chem. Abs.*, 1912, 6, 1377. British P. 3496 and 3497, 1911; *J.S.C.I.*, 1912, 31, 347. French P. 429,292, 1911; *J.S.C.I.*, 1911, 30, 1267. See also B. B. Goldsmith, British P. 6396, 1912; *J.S.C.I.*, 1913, 32, 456.

<sup>77</sup> H. Moschatos and B. Tollens, *Ann.*, 1893, 272, 280; *Ber.*, 1891, 24, 695; 18'4, 27, 238. H. Lebach, *Z. angew. Chem.*, 1909, 22, 1600; *J.S.C.I.*, 1913, 32, 559. M. T. Harvey and L. H. Baekeland, *Ind. Eng. Chem.*, 1921, 13, 135. J. E. Laborde, *Chimie et industrie*, 1929, Feb. Special No., 504; *Chem. Abs.*, 1929, 23, 4188.

<sup>78</sup> L. H. Smith and K. N. Welch, *J.C.S.*, 1934, 729.

<sup>79</sup> J. C. Duff and E. J. Bills, *J.C.S.*, 1934, 1305.

The stability of the phenol-hexamine bodies has been studied by Pummerer and Hofmann.<sup>80</sup> In water or benzene the compounds reverted to their components. Union of phenol and hexamine is effected by mixing them in the presence of a little alcohol. Lebach<sup>81</sup> and also Sugimoto<sup>82</sup> noted that hexamine triphenol evolved ammonia when heated to yield an insoluble infusible mass similar to Bakelite C.

Redman, Weith and Brock<sup>83</sup> found that hexamethylenetetramine was decomposed completely by boiling in dilute aqueous hydrochloric acid, though alkalis had no effect. When the compound of hexamine and phenol was heated, methylamine as well as ammonia was given off. Dry heating at 175°C. for 1 hour resulted in a resin attacked both by solvents and dilute acid. By adding phenol so that the molecular proportion of formaldehyde to phenol was 7 to 6, no longer were methylamines evolved, but only ammonia. This indicated a complete combination of the formaldehyde with the phenol. When phenol was added beyond the 7:6 ratio, the excess could always be separated on completion of the reaction and the resin was believed to be identical with that resulting from the 7:6 ratio. Amino-saligino-saligenin,  $\text{HOC}_6\text{H}_4\text{OCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{NII}_2$ , was isolated as an intermediate, but at the end of the reaction no such substances could have been present, as all of the nitrogen was accounted for in ammonia evolved. It was suggested that a long saligino-saligenin chain constituted the initial soluble resin (Novolak). Analysis agreed with the formulation of  $\text{C}_6\text{H}_5\text{OCH}_2(\text{C}_6\text{H}_4\text{OCH}_2)_n\text{C}_6\text{H}_4\text{OH}$ . Transformation into an infusible insoluble resin required condensation with additional active methylenes. Another conclusion which was reached from a study of the hexamine resins was that their superior light-fastness indicated a possible freedom from hydroxyl groups, a conclusion supported by the fact that very prolonged treatment with caustic soda was necessary before signs of attack could be observed.

Sato and Sekine<sup>84</sup> found that phenol-formaldehyde condensations catalyzed by ammonia could be fractionated into three components by virtue of their different solubilities. Megson and Drummond<sup>85</sup> observed this same property in m-cresol condensations catalyzed by caustic soda and these fractions also had different heat hardening rates. Duff and Bills<sup>86</sup> reported that when hexamine and salicylic acid were heated in aqueous solution, 3- and 5-aldehydosalicylic acids were obtained (and separated by their differing solubilities in benzene) instead of the expected methylalsalicylic acids. m- and p-Hydroxybenzoic acids gave only amorphous products. Shono<sup>87</sup> isolated a light yellow amorphous powder, whose analysis indicated  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}$ , from a phenol-formaldehyde condensation catalyzed by a large amount of ammonia. Other compounds<sup>88</sup> isolated were 2,2'- and 4,4'-dihydroxydibenzylamines melting at 168°C. and 137-138°C., respectively. At higher condensation temperatures (140°C.) a compound,  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{N}$ , stated to be  $\omega$ -amino-o-tolyl-o-hydroxybenzyl ether was formed.

Marotta and Alessandrini<sup>89</sup> also studied the reaction between phenols and hexamine in acetic acid solution and they suggested that hexamine is first oxidized to trihydroxytrimethylamine, which in turn condenses with the phenol.

<sup>80</sup> R. Pummerer and J. Hofmann, *Ber.*, 1923, 56, 1257.

<sup>81</sup> H. Lebach, *Z. angew. Chem.*, 1909, 22, 1600; *Chem. Abs.*, 1910, 4, 391.

<sup>82</sup> S. Sugimoto, *Rep. Osaka Imp. Inst. Ind. Res.*, 1927, 8, (17); 1931, 11, (21); *Chem. Abs.*, 1928, 22, 142; 1931, 25, 3778; *Japanese P.* 83,652; *Chem. Abs.*, 1931, 25, 3778.

<sup>83</sup> I. V. Redman, A. V. Weith and F. P. Brock, *Ind. Eng. Chem.*, 1914, 6, 3.

<sup>84</sup> S. Sato and Y. Sekine, *J. Chem. Ind. (Japan)*, 1921, 24, 332; *Chem. Abs.*, 1922, 16, 1133.

<sup>85</sup> N. J. L. Megson and A. A. Drummond, *J.S.C.I.*, 1931, 50, 251T.

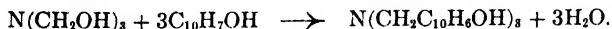
<sup>86</sup> J. C. Duff and E. J. Bills, *J.C.S.*, 1932, 1987.

<sup>87</sup> T. Shono, *J. Chem. Ind. (Japan)*, 1926, 29, 53, 438; 1927, 30, 136; *Chem. Abs.*, 1926, 20, 2419; 1927, 21, 628, 1335.

<sup>88</sup> T. Shono, *J. Chem. Ind. (Japan)*, 1929, 32, 212; *Proc. World Eng. Congr.*, 1929, 31, 533; *Chem. Abs.*, 1930, 24, 1940.

<sup>89</sup> D. Marotta and M. E. Alessandrini, *Gazz. chim. ital.*, 1931, 61, 977; *Chem. Abs.*, 1932, 26, 2963.

Phenol, resorcinol, phloroglucinol and naphthols all gave products which were difficult to purify and which became plastic masses when warmed or exposed to air. Naphthols gave bases, by reactions formulated as:



Resins made from phenol and hexamethylenetetramine<sup>80</sup> were found to be infusible whenever the methylene to phenol ratio in the resin was greater than 0.5 to 1. Therefore the only fusible intermediates are dinuclear. A different result was obtained by starting with saligenin, in which case polynuclear fusible resins were obtained, along with infusible resins which contained at least 11 molecules. It was suggested that the resins consist of mixtures of open chain as well as ring systems.

The effects of amines other than hexamethylenetetramine in causing reaction of phenols with formaldehyde are discussed in Chapter 16. The mechanism of these catalyses presumably varies from case to case and it is difficult to make any generalizations. The statement can be made, however, that crystalline products which may be intermediates have often been encountered. Thus, from monophenols and formaldehyde in the presence of dimethylamine, compounds of the type  $\text{o-HOC}_6\text{H}_4\text{CH}_2\text{N}(\text{CH}_3)_2$  were obtained.<sup>81</sup> Phloroglucinol condensed with formaldehyde and dimethylamine hydrochloride to yield  $(\text{HO})_3\text{C}_6\text{H}_2\text{N}(\text{CH}_3)_2\cdot\text{HCl}$  and  $(\text{HO})_3\text{C}_6\text{H}[\text{CH}_2\text{N}(\text{CH}_3)_2\cdot\text{HCl}]_2$ . These hydrochlorides gave resins when treated with alkali. Aminophenols and aldehydes gave substituted methyleneaminophenols.<sup>82</sup>

#### PHYSICO-CHEMICAL STUDIES OF PHENOL-FORMALDEHYDE RESINS

Sato and Sekine<sup>83</sup> have called attention to the amphoteric nature of phenol-formaldehyde resins. When the alkaline condensation products of phenol and formaldehyde are washed till neutral to litmus, and then dissolved in acetone, the addition of a comparatively large amount of alkali is necessary to render the solution alkaline to phenolphthalein, yet more than an equivalent of acid is necessary to turn the same solution acid to congo red. A characteristic dark yellow substance is formed when copper sulphate is introduced into the condensation product, but there is no blue coloration when ammonia is added. The yellow color was discharged by lactic acid. Copper carbonate, however, gave a brown product unaffected by lactic acid. The amphoteric nature of these resins is considered to be due to the presence of both aromatic and aliphatic hydroxyl groups. The investigators deduce that the resin molecules should combine with compounds containing an aliphatic hydroxyl group. Sato<sup>84</sup> confirmed this by preparing insoluble resinous material from the condensation of the oily reaction product of equimolecular parts of phenol and formaldehyde, with malic, lactic or glycollic acid, butyl alcohol, glycerol, cholesterol and hexoses.

Shono<sup>85</sup> recorded 40 metallic salts which would react with phenol resins in alcohol solution. The chlorides of cobalt, iron, vanadium, selenium, titanium, ruthenium and tungsten, uranium nitrate, various chloroaurates and chloroplatinates gave characteristic colors. These color reactions served as a means of differentiating this type of synthetic resin and natural resins. The action of condensation products derived from polyhydric phenols and formaldehyde on aqueous solu-

<sup>80</sup> G. Walter and G. Reimer, *Kolloid-Beihfte*, 1934, 40, 1, 29, 45; *Brit. Chem. Abs. B*, 1934, 1021.

<sup>81</sup> J. Decombe, *Compt. rend.*, 1933, 197, 258; *Chem. Abs.*, 1933, 27, 5065. *Compt. rend.*, 1933, 196, 544; *Brit. Chem. Abs. A*, 1929, 1440.

<sup>82</sup> T. G. Levi, *Gazz. chim. ital.*, 1929, 59, 544; *Brit. Chem. Abs. A*, 1929, 1440.

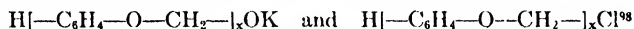
<sup>83</sup> S. Sato and Y. Sekine, *J. Chem. Ind. (Japan)*, 1921, 24, 494; *Chem. Abs.*, 1922, 16, 1133.

<sup>84</sup> S. Sato, Japanese P. 37,857 and 39,321, 1921; *Chem. Abs.*, 1922, 16, 1301, 2760. British P. 182,886, 1921; *J.S.C.I.*, 1922, 41, 676A.

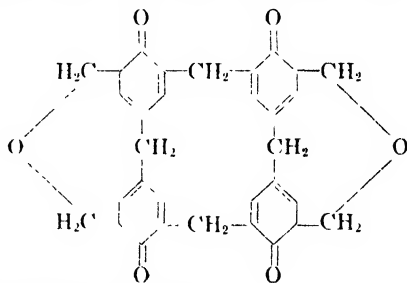
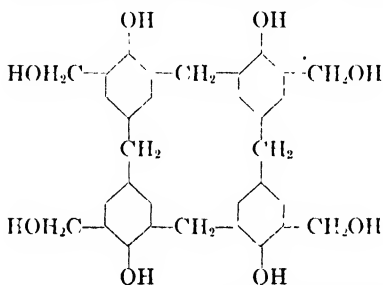
<sup>85</sup> T. Shono, *J. Chem. Ind. (Japan)*, 1926, 29, 53; *Chem. Abs.*, 1926, 20, 2419.

tions of metallic salts was studied by Adams and Holmes.<sup>96</sup> The resins exhibited pronounced and selective adsorptive properties for a large number of cations (e.g.,  $\text{Al}^{+++}$ ,  $\text{Ca}^{++}$ ,  $\text{As}^{+++}$ ,  $\text{Pb}^{++}$ ,  $\text{Sn}^{++}$  and  $\text{V}^{++}$ ). As a result of their experiments the investigators recommended the use of such resins as pyrocatechol-formaldehyde, resorcinol-formaldehyde, pyrogallol-formaldehyde and quebracho tannin-formaldehyde for the purification of water.

The behavior of alcoholic suspensions of resins under the influence of an electric field was investigated by Barthélemy.<sup>97</sup> Alkaline-catalyzed resins were found to migrate to the cathode, and acid-catalyzed ones to the anode. He regarded them therefore as ionic micelles having the constitution:



The growth of colloidal aggregates presumably occurs through the ionic nature of these particles. Ripper,<sup>99</sup> comparing Barthélemy's formulation with the structures mentioned by Raschig<sup>100</sup> and Herzog,<sup>101</sup> suggests that in the final resin the value



Possible structures existing within ionic micelles

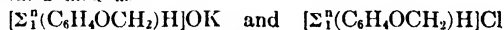
of  $n$  is greater than 4, since structures as shown above probably would not display colloidal properties. Nagel and Baumann<sup>102</sup> find that the reaction mechanism for the hardening of phenol-formaldehyde resins involves the formation of large molecular aggregates without the elimination of any water (with shellac a little is formed). These investigators were unable to find evidence for any chemical reaction taking place during hardening. The sizes of colloidal resin particles<sup>103</sup> range from the smallest which can be detected by means of the ultramicroscope to the largest which are present in partial suspensions.

It is known that resin-forming reactions are facilitated by stirring.<sup>104</sup> Freundlich and Kroch<sup>105</sup> have shown that stirring coagulates copper oxide sols, indicating that orientation and aggregation can be accomplished by this means. According

<sup>96</sup> B. A. Adams and E. L. Holmes, *J. S. C. I.*, 1935, 54, 17

<sup>97</sup> H. Barthélemy, *Chim. et ind.*, 1926, 16, 367; *Rev. prod. chim.*, 1925, 28, 261; *Kunststoffe*, 1925, 15, 150; *Chem. Abs.*, 1925, 19, 2552

<sup>98</sup> Barthélemy represented these as



<sup>99</sup> K. Ripper, *Kontakt-Römmeler Nach.*, 1929, 1, 4

<sup>100</sup> P. Raschig, *Z. angew. Chem.*, 1912, 25, 1446; *Chem. Abs.*, 1913, 7, 887

<sup>101</sup> W. Herzog and J. Kieidl, *Z. angew. Chem.*, 1922, 35, 643; *Chem. Abs.*, 1923, 17, 1722

<sup>102</sup> W. Nagel and E. Baumann, *Wiss. Veröffentl. Siemens-Konzern*, 1932, 11, 99; *Chem. Abs.*, 1933, 27, 856. See also J. Scheiber, *Farbe u. Lack*, 1927, 67, 1929, 86, 102; *Chem. Abs.*, 1927, 21, 1555; 1929, 23, 2583, 5599.

<sup>103</sup> H. L. Bender, "Colloid Chemistry," J. Alexander, The Chemical Catalog Company, New York, 1932, IV, 332. R. Dubray, *Chimie et industrie*, 1928, (April Special No.) 666; *Chem. Abs.*, 1928, 22, 4842; *Rev. gen. mat. plast.*, 1927, 3, 285; *Chem. Abs.*, 1927, 21, 2991. See also Chapter 4.

<sup>104</sup> A. W. C. van Voorhout, U. S. P. 1,271,392 and 1,271,393, July 2, 1918; *Chem. Abs.*, 1918, 12, 1916. British P. 110,041, 1916; *Chem. Abs.*, 1918, 12, 410. French P. 423,417, 1917; *Chem. Abs.*, 1918, 12, 983.

<sup>105</sup> H. Freundlich and H. Kroch, *Naturwissenschaften*, 1926, 14, 1206; *Chem. Abs.*, 1927, 21, 1394. *Z. phys. Chem.*, 1926, 124, 154; *Chem. Abs.*, 1926, 20, 845.

to Ostwald<sup>106</sup> the effect is due to potential differences set up between the stirrer and the colloid system. Exposure of Bakelite to a concentrated electric field was reported to have catalyzed hardening of the resin. The effect was assumed to be due to changes in the energy content of the particles.<sup>107</sup> Jablonower<sup>108</sup> found that the density of a phenol-formaldehyde condensation catalyzed by ammonia, increased steadily with the time of heating and the proportion of catalyst used.

While the advanced stages of the phenol-formaldehyde reaction involve the aggregation of colloids, the initial syrups are merely mixtures of crystalline substances which necessarily lower each other's melting points, and which are supercooled liquids. This was demonstrated by Drummond<sup>109</sup> through the use of viscosity measurements. Initial syrups obtained by alkaline condensation of phenol with formaldehyde obeyed Slotte's law for the variation of viscosity with temperature:  $\eta = K/t^n$ , where  $t$  is in degrees Fahrenheit. The law does not hold for colloids.<sup>110</sup> This observation of Drummond that the logarithm of the viscosity of the initial resin varied linearly with temperature has been confirmed.<sup>111</sup> Warren, Newbound and Bell<sup>112</sup> suggested that automatic control of condensations might well be based on viscosity measurements.

Novak and Cech<sup>113</sup> decided that since intermediate stages in the formation of resins from the reaction of phenol with formaldehyde were difficult to isolate, it might be possible to study them by determining the refractive index, the viscosity in alcohol and the bromine value (by Koppeschaar's Method) of the filtrate which remained after precipitating an acetic acid solution of the resin with water. They studied various types of condensation, including (1) uncatalyzed, (2) catalyzed by ammonia, (3) catalyzed by caustic soda. Condensation phenomena were manifested by decrease in the bromine value and in the refractive index of the aqueous layer, while polymerization was indicated by increase in refractive index of the resin layer and partly by increased viscosity.

Schmid and de Senarcens<sup>114</sup> followed the change in refractive index (using yellow helium light of 5876Å) during the conversion of resin A to resin C in the presence of varying amounts of caustic soda ranging from 1.07 to 2.66 per cent at 100-140°C. The values they obtained for any one set of conditions increased rapidly at first and then more slowly until the maximum was reached. Increases in the concentration of caustic soda lowered the maximum value of the refractive index. The data indicated that polymerization proceeded at the same time as did condensation and that polymerization was not affected by the alkali.

Sugimoto and Kasai<sup>115</sup> investigated the absorption spectra of phenol-formaldehyde products prepared without catalysts, and a band was found only in the ultraviolet. Using ammonia as catalyst there appeared bands which were traced to the presence of a decomposition product of hexamnetriphenol. The red color formed in Bakelite in the course of time was shown to be due to a triphenyl-methane dye (aurin).

<sup>106</sup> W. Ostwald, *Kolloid-Z.*, 1927, 41, 71; *Chem. Abs.*, 1927, 21, 3516

<sup>107</sup> British P. 417,501, 1934, to Ternion A.-G., *Chem. Abs.*, 1935, 29, 1178. See Chapter 9

<sup>108</sup> B. Jablonower, *J.A.C.S.*, 1913, 35, 811.

<sup>109</sup> A. A. Drummond, *J.S.C.I.*, 1922, 41, 522T; 1924, 43, 323T; 1923 42, 770T.

<sup>110</sup> C. E. Davis and E. T. Oakes, *J.A.C.S.*, 1922, 44, 477.

<sup>111</sup> A. D. Sokolov, S. R. Pliad and N. V. Gregor'eva, *Plasticheskie Massui*, 1934, 3, 32; *Chem. Abs.*, 1934, 28, 6579. P. A. Kremlevskii, *Zavodskaya Lab.*, 1933, 5, 16; *Chem. Abs.*, 1933, 27, 5993. B. A. Lomakin and N. I. Kutoyova, *Plasticheskie Massui*, 1934, 3, 25; *Chem. Abs.*, 1934, 28, 6579. See also Chapter 3.

<sup>112</sup> H. W. H. Warren, R. Newbound and L. M. T. Bell, British P. 253,614, 1925, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.*, 1926, 681.

<sup>113</sup> J. Novak and V. Cech, *Ind. Eng. Chem.*, 1928, 20, 796; 1932, 24, 1275.

<sup>114</sup> A. Schmid and G. de Senarcens, *Helv. Chim. Acta*, 1933, 16, 10; *Brit. Plastics*, 1933, 5, 134; *Chem. Abs.*, 1933, 27, 2049.

<sup>115</sup> S. Sugimoto and E. Kasai, *Repts. Imp. Ind. Res. Inst. Osaka, Japan*, 1927, 7, (14); *Chem. Abs.*, 1927, 21, 2172.



Boer, Houwink and Custers<sup>116</sup> studied the absorption curve of a phenol-formaldehyde resin and found that it was similar to that of phenol but approximated that of cresol in that it was displaced towards the red. This was considered to be a striking confirmation that the structure is  $(\text{CH}_2\text{C}_6\text{H}_4\text{OH})_x$ . Molecular refraction measurements had increased values as condensation between phenol and formaldehyde proceeded, an increase related quantitatively to the absorption displacement towards the red.

Stäger<sup>117</sup> prepared resins by reacting formaldehyde in the presence of ammonia with three different sources of phenols, viz., pure phenol, cresol and mixtures of phenol with cresol. Eleven specimens of resin in all were examined. Their specific gravity at 20°C. ranged from 1.18 to 1.24. The resins had melting points of about 59-67°C. and bromine absorption of 0.32-0.53 g. per g. of resin. Cementing values towards steel were obtained with reference to the time of hardening and many electrical tests were carried out, the investigator concluding that products derived from formaldehyde and pure phenol have definite polar characteristics. The cresol derivatives have comparatively high molecular weight and are non-polar. Stäger noted also<sup>118</sup> that when the resins were heated at 100°C. for considerable periods of time, thus forming stage C, the volatile material obtained consisted chiefly of water and phenols.

#### SUMMARY

In the preceding pages the reactions of formaldehyde and phenols have been discussed and mention has been made of aldehydes other than the simple formaldehyde. Various views as to the mechanism of these condensations have been examined and a certain amount of general agreement has been found among them. Yet the significance of the fact that phenol-formaldehyde condensation products polymerize under definite conditions of time, temperature and pressure has not been fully elucidated. The main facts established are these:—

1. The initial reaction of phenols and formaldehyde results in the formation of compounds of the alcohol type or of the diarylmethane type or a combination of both.
2. These compounds react further to form extended molecules which may be regarded as joined substituted benzyl groups possessing oxygen or carbon linkages.
3. The chains or *branchiae* particularly in the presence of some slight excess of formaldehyde and a basic catalyst can be transformed irreversibly into insoluble, infusible material, most probably by polymeric change.

<sup>116</sup> J. H. de Boer, R. Houwink and J. F. H. Custers, *Rec. trav. chim.*, 1933, 52, 709, *Chem. Abs.*, 1933, 27, 5004.

<sup>117</sup> H. Stäger, *Helv. Chim. Acta*, 1931, 14, 285, *Chem. Abs.*, 1931, 25, 3183.

<sup>118</sup> H. Stäger, 1st Communication New Inter Assoc. Testing Materials Zurich, 1930C, 19; *Chem. Abs.*, 1931, 25, 3411.

## Chapter 15

### Phenol-Aldehyde Resins

#### III. Commercial Processes

During the first decade of the present century activity greatly increased in the study of phenol-aldehyde resins and their applications as substitutes for shellac and other resins in both varnishes and plastic compositions. In the latter part of that decade, Baekeland began an investigation which brought forth a modification of these resins by improving the methods of hardening under heat and pressure so that rigid molded articles could be very readily obtained. From his investigations came the commercial development of the molding composition and product known in its various forms as Bakelite. A great variety of applications have been made of these phenol-formaldehyde resins or resinoids ranging from bottle closures to telephone hand-sets; from table tops to artificial amber. The range of uses also embraces such articles as molded cases and parts for cameras, clocks and precision instruments, armatures and commutators for dynamos and motors, automobile parts, electrical equipment, grinding wheels, toilet seats, serving trays, soda-fountain counters, scale pans, golf clubs and containers of many kinds. The commercial success of this material has been a powerful stimulant to the development of the industry of synthetic plastics.

To a notable extent the applications of phenol-formaldehyde resins in the plastics field have been spectacular and during the period of commercial development and expansion they have therefore been particularly before the public eye. Such varied applications as radio apparatus, pencil barrels, ash trays and other articles constantly in evidence give some indication as to the importance of these resins for which accurate consumption data are not available.<sup>1</sup>

In the United States, the production of molding compositions was practically restricted to one corporation, the rights of manufacture having been closely retained by the owners of the principal patents.<sup>2</sup> Since the expiration of some of the original patents (1926), a number of other manufacturers have become firmly established in the United States.

In the past, the molder requiring such compositions purchased his raw material at a price roughly representing one-half the cost of the molded article, that is, the costs of the composition and of labor were about equal. With increasing competition the prices of molding compositions gradually decreased. Simultaneously

<sup>1</sup> Accurate production figures for phenol-formaldehyde resins have been largely withheld. However, it has been estimated that in the United States in 1921 the production was between 2000 and 3000 tons; in 1928, it was about 10,000 tons. [A. Marcus, *Chem. Age (London)*, 1929, 20, 538]. According to L. V. Redman (*Chem. Markets*, 1929, 24, 481), in the decade 1919-1929 there was a tenfold volume increase.

<sup>2</sup> During the early stages of L. H. Baekeland's commercial development, J. W. Aylsworth and L. V. Redman independently began the manufacture of the related products, Condensite and Redmanol respectively, and in 1916 a controversy took place between Baekeland, Redman (and his associates, A. J. Weith and F. P. Brock) and K. Brown (as Aylsworth's successor), partly over the bearing of Redman's process on Baekeland's inventions. (See *Ind. Eng. Chem.* 1911, 3, 439, 518; 1914, 6, 3, 167, 263; 1916, 8, 177, 473, 568, 1077, 1171; 1917, 9, 207.) After much litigation a consolidation of these competitive interests was effected (see *Chem. Met. Eng.* 1922, 25, 279; 1923, 26, 996, 1184) and the products Bakelite, Condensite and Redmanol, were placed under the control of the Bakelite Corporation.

with the expiration of the original patents, a number of molders started and have continued manufacturing their own materials. This private manufacture<sup>3</sup> has been based largely on the need for smaller quantities of resins which are better suited for particular purposes.

In view of the publicity given phenol-formaldehyde resins and their uses in a number of striking ways, there has been a possibly unwarranted amount of activity among research workers in adding to, modifying, and transforming them. It has even been thought advisable by Stone<sup>4</sup> to familiarize chemistry students with this field by including an experiment on the preparation of a resin from phenol and paraformaldehyde in their training. The result of this extensive interest has been a large amount of published work whose study presents no small task to one desirous of becoming familiar with the field. An attempt is made here to review all of the available published material, and it is believed that in the following pages a very complete survey will be found. However, space limitations prevent extended review of all references and the present objective has been rather to indicate the keynote of any particular investigation and to give those wishing to pursue the subject further guidance to the original literature.

If more of the zeal which has been put into the study of modifying phenol-formaldehyde resins or of making additions to them for the purpose of accomplishing only a minor change in physical characteristics had been applied to such problems as control in manufacture, acceleration of the molding operation, production of a pure white molding composition, improvement in the strength and appearance of cold-molded products without greatly adding to their cost, elimination of odor and of the disadvantage of darkening under light, production of more flexible moldings, reduction of trouble and time required for casting, formation of castings which will not shrink on cooling, or other problems mentioned by Spencer and Murray,<sup>5</sup> it is safe to say that a greater measure of progress would have been made in the field of resinous plastics.

The condensation products of phenols and aldehydes include a wide range of substances but comparatively few of these are resinous. Of these, a still smaller number are worth considering as practical substitutes for natural resins or for use in molding compositions. Phenol itself and m- and p-cresol yield useful resins with formaldehyde but the corresponding compound of o-cresol is practically useless in thermosetting molding compositions and it must be separated with great care from crude cresol. Higher homologues of phenol produce increasing proportions of inert, non-resin-forming or crystalline bodies as the molecular weight increases.

Many terms have been used to describe the resinous condensation products of phenols and formaldehyde<sup>6</sup> so that much confusion exists. In the present discussion the various names urged by different investigators have been largely omitted from the text; the longer terms, soluble fusible resin and insoluble infusible resin, have been preferred for the sake of clarity.

<sup>3</sup> For a discussion of the plant, labor and materials required in the manufacture of phenol-formaldehyde resins, see W. McHutchison, *Industrial Chemist*, 1934, 10, 383.

<sup>4</sup> C. H. Stone, *J. Chem. Ed.*, 1930, 7, 1663.

<sup>5</sup> D. A. Spencer and H. D. Murray, *J.S.C.I.*, 1927, 46, 637

<sup>6</sup> The terms "resol," "resitol," "resite" and "novolak" are often used. A resol is a resin of the type hardenable by heat to a final infusible and insoluble condition but reacted only to the stage where it still melts when heated and is soluble in acetone; this is also known as the A or "treacle" stage. A *resitol* is a resin of the same type as a resol but further reacted to a B stage where it has become infusible, i.e., it does not melt though it softens decidedly on heating, and it is insoluble but swells in acetone. A *resite* is the same heat-hardenable resin but reacted to the final or C stage, characterized by complete insolubility in acetone and infusibility without any material softening upon heating. A *novolak* is a distinctly different type of resinous reaction product in that practically speaking it does not harden upon heating to an insoluble infusible condition but remains soluble and fusible. A general term for phenol condensation products is "phenoplast."

## MANUFACTURING PROCESSES

In the manufacture of phenol-formaldehyde resins or resinoids (see Chapters 1 and 14) either wet or dry processes (so-called) may be used. The former are based on the use of aqueous formaldehyde, and the latter substitute solid aldehydes (paraformaldehyde, hexamethylenetetramine or similar aldehyde-yielding reagents) for the solution. On account of the expense of anhydrous aldehyde, dry processes are generally used only for the preparation of transparent, translucent or opalescent, light-colored cast or turned<sup>7</sup> articles such as cigar and cigarette holders, umbrella handles, dentures, amber substitutes, beads and similar ornamental objects where the cost of raw materials is less vital than with cheaper molding compositions.

In the wet process, the formaldehyde may be introduced all at once, or it may be added in two stages. For convenience, the two-stage processes will be discussed separately from the one-stage processes, although there is no very definite distinction between them.<sup>8</sup> In both cases, the resin is subjected to heat and pressure in the mold in order to convert it into an infusible insoluble product.

**Two-Stage Wet Processes.** These processes, giving reasonably uniform results, have found favor from a manufacturing standpoint and will therefore be discussed first. Resins made by the one-stage wet process can be expected to be slightly cheaper than those made by a two-stage process, especially when the latter requires the use of anhydrous aldehyde.

In the operation of the two-stage wet processes, a fusible, soluble resin is first formed and then dehydrated in the same reaction kettle. These resins are usually brittle and can be ground for mixing with the anhydrous aldehyde hardening agent. Fillers, coloring materials and other ingredients (if desired) are added at this point. It is possible to determine the optimum time<sup>9</sup> at which to stop stage one by the use of physical tests (hardness and fluidity). Methods for carrying out these tests are described in Chapter 69. The product may then be worked up into a form for molding under heat and pressure.<sup>10</sup>

Baekeland<sup>11</sup> obtained products in this way which when molded were similar to hard rubber or ivory, insoluble in alcohol and acetone, and resistant to heat, moisture and most chemical reagents. Phenol or cresol is treated with about an equal volume of commercial formaldehyde solution (this being approximately equivalent to the phenol molecularly) or a slight excess of the formaldehyde may be used. On heating, with or without catalytic bodies, reaction takes place and a heavy oily viscous layer separates from the aqueous solution. The aqueous layer is rejected and the syrupy liquid, which is soluble in alcohol and acetone, may be heated on a steam bath to thicken it slightly and to drive off any remaining water. If the reaction is permitted to proceed further the product may become gelatinous. At this stage the resin is incompletely soluble in alcohol but more readily soluble in acetone. Heating converts it into a heat-resistant body. Various

<sup>7</sup> The term, "turnery" resins; has been used to designate those which are capable of being worked on lathes and similar devices.

<sup>8</sup> It is evident that almost limitless variations from true one-stage to true two-stage processes are possible, depending upon the quantity of aldehyde required for hardening, and that the differentiation between the two types is not a sharp one.

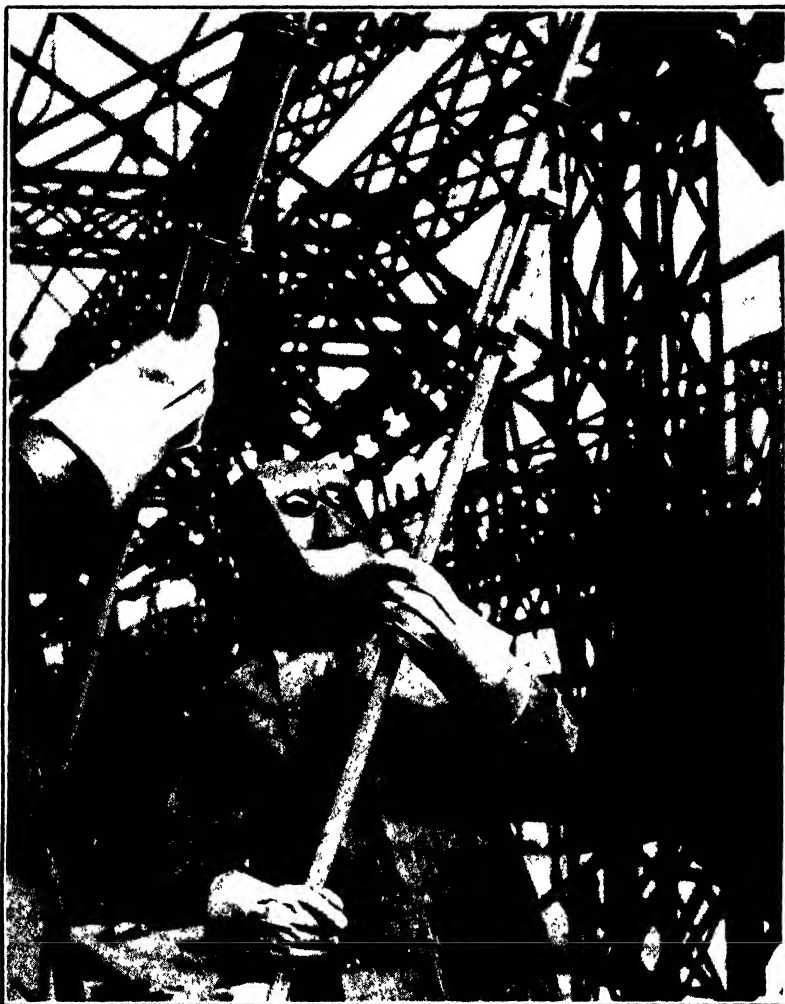
<sup>9</sup> M. Koebner, U. S. P. 1,981,514, Nov. 20, 1934, to F. Raschig, G.m.b.H.; *Chem. Abs.*, 1935, 29, 526.

<sup>10</sup> British P. 416,847, 1933, to F. Raschig, G.m.b.H.; *Brit. Chem. Abs.* B, 1934, 1022.

<sup>11</sup> *Chem. Age (London)*, 1926, 14, 72, 345.

<sup>12</sup> L. H. Baekeland, U. S. P. 942,659, Dec. 7, 1909; *Chem. Abs.*, 1910, 4, 680. This patent, commonly called the "heat and pressure patent," has been involved in litigation; U. S. Dist. Court, Eastern Dist. of New York, *General Bakelite Co. vs. General Insulate Co.* The patent was held valid. Another case involving its validity was won by the General Bakelite Co. against the Brunswick-Balke-Collender Co. Since the expiration of this basic patent a great deal of competition has opened up in the industry.

fillers (asbestos, wood fiber, rubber, zinc oxide, barium sulphate, calcium sulphate, graphite, horn, bone, starch, pumice and many others have been used) and modifying agents, including resins, nitrocellulose and casein, may be added.



*Courtesy Bakelite Corp.*

**FIG. 58.—Laminated Phenol Plastic Tubing Used for High Voltage Detectors on Power Lines.**

On heating under pressure at 110-140°C., a hard compact molded article is obtained in 1-2 hours.<sup>12</sup> Baekeland observed that various catalysts, such as acids<sup>13</sup> or salts, including zinc chloride and calcium chloride, could be used advantageously.

Baekeland<sup>14</sup> prepared a solid partial reaction product of phenol and formaldehyde to which could be added a filler (e.g., wood flour), ground it, molded it

<sup>12</sup> Present practice reduces the molding time considerably.

<sup>13</sup> Acid condensing agents are not looked upon with favor by commercial molders because of possible corrosion of the molds

<sup>14</sup> L. H. Baekeland, U. S. P. 939,966, Nov. 16, 1909; *Chem. Abs.*, 1910, 4, 680.

under pressure, and by heating at 100-200°C., transformed the resin into an insoluble and infusible condensation product. He suggested a great variety of fillers, including asbestos fiber, other fibrous or cellular materials, rubber, casein, lampblack, mica, mineral powder such as zinc oxide or barium sulphate, pigments, dyes, nitrocellulose, abrasive materials, lime, calcium sulphate, graphite, cement, powdered horn, bone, pumice stone, talc, starch and resins. Wood flour, however, is especially useful to retard shrinkage and minimize brittleness.

To produce shaped or molded articles without keeping the material in molds during the entire hardening operation, Baekeland<sup>15</sup> made an initial condensation product from approximately equal volumes of ordinary commercial formalin and phenol or cresol, separated the water and subjected the oily or viscous material to gentle heating to transform it into an intermediate product which was solid at all temperatures. This product is more or less hard when cold but becomes elastic and capable of yielding to pressure when slightly heated, resuming its original shape if the pressure be discontinued. In this form the material is insoluble in alcohol and glycerol but swells in phenol or acetone. These properties are utilized by heating the initial product in molds until the intermediate product is formed, removing the shaped masses from the mold and subjecting them to further heat treatment to bring about hardening, as heat may be applied under these conditions without danger of deformation. By this procedure the molds are quickly available for further work. The molded articles in the intermediate stage of conversion may be hardened by baking at low temperatures in an inert gas at atmospheric or higher pressures. The process enables the formation of large blocks free from gas bubbles or pores.

The discovery of the value of hexamethylenetetramine in the preparation of phenol-formaldehyde products (see Chapter 14) contributed largely to the extensive utilization of phenolic resins. No adequate substitute has yet been found for this almost ideal hardening agent. It acts as a flux, thereby assisting in the formation of shaped articles. Furthermore, it breaks down giving ammonia, which acts as a catalyst, and methylene groups, which are required for the final hardening. A small percentage of hexamethylenetetramine is sufficient to act as a "trigger" in causing additional formaldehyde to react with the soluble resin. Rapid cures are obtained in this manner (see Chapter 26). In Aylsworth's<sup>16</sup> process a phenol resin is first made in which the proportion of formaldehyde is such that the resin is permanently fusible. This may be heated to 215°C. or higher (a temperature of 200°C. is necessary to remove all free and combined water) and consequently it can be completely dehydrated. Dehydration of partial condensation products which become infusible on further heating could not, of course, be carried out in this manner. To form the final infusible product the dehydrated resin is combined with hexamethylenetetramine or paraformaldehyde. One advantage of using hexamethylenetetramine is that the reaction is more nearly anhydrous, ammonia being evolved but no water or formaldehyde as with paraformaldehyde. No counteracting pressure is needed and the ammonia given off may be rendered harmless by an added substance such as an organic acid anhydride. An entirely anhydrous commercial product of this character would be of special value, according to Brown,<sup>17</sup> where products of high dielectric strength are desired.

Another proposal by Aylsworth<sup>18</sup> particularly emphasized forming fusible phenol-formaldehyde resins with the careful exclusion of catalysts. The ingredients (for

<sup>15</sup> L. H. Baekeland, U. S. P. 942,700, Dec. 7, 1909; German P. 237,790, 1908; *Chem. Abs.*, 1910, 4, 680.

<sup>16</sup> J. W. Aylsworth, U. S. P. 1,020,593, March 19, 1912; *J.S.C.I.*, 1912, 31, 399.

<sup>17</sup> K. Brown, *Ind. Eng. Chem.*, 1916, 8, 1172.

<sup>18</sup> J. W. Aylsworth, U. S. P. 1,102,630, July 7, 1914; *J.S.C.I.*, 1914, 33, 931.

example, 1000 parts by weight of phenol and 750 parts of a 35 per cent formaldehyde solution) are heated in a closed vessel at 150-160°C. without a condensing agent. In fact, Aylsworth stated that any impurity which will act as an accelerator or catalytic agent should be eliminated. For this reason iron and lead vessels are not suitable, but well-enameled or tinned iron and tinned copper or nickel have no objectionable action. The phenol or cresol should be carefully refined to eliminate basic metallic impurities as well as mineral acids. Aylsworth<sup>19</sup> also produced a hard infusible material from a resinous fusible condensation product of phenol and formaldehyde (dehydrated and freed from uncombined formaldehyde) and hexamethylenetetramine, the mixture being heated sufficiently at about 95-115°C. to cause reaction. The hexamethylenetetramine is used in a quantity at least sufficient to combine with all the fusible condensation product and free phenol contained in it. The fusible resin may contain 3 mols of phenol to 2 mols of formaldehyde or equivalent, and to it 7.6 to 12 per cent of hexamethylenetetramine is added.

A somewhat more complicated method of preparing molding compositions was also proposed by Aylsworth<sup>20</sup>. A fusible phenol-formaldehyde resin is dissolved in an alkaline solution. The alkali may be the hydroxide of sodium, potassium, barium or calcium. Fibrous fillers are then added. The alkali subsequently is neutralized by addition of an acid. When the alkali is sodium or potassium hydroxide the neutralizing agent may be stearic acid or rosin. If the basic reagent is calcium or barium hydroxide, an acid (sulphuric, oxalic or carbonic) which forms an insoluble compound may be used. The neutralization of the alkali precipitates the resin together with any insoluble salts which may be formed and the composite mass is dried and used for molding purposes. Hexamethylenetetramine may be added to bring about reaction in the mold. Aylsworth mixed 100 parts of resin with milk of lime formed by the hydration of 24 to 28 parts of calcium oxide with 300 to 600 parts of water. The mixing step is continued until the phenolic resin has completely entered into solution, which takes 12-36 hours. The liquid is then thoroughly incorporated with 70 to 300 parts filling material (wood flour, asbestos fiber, cotton flock or powdered mineral material). The mass is exposed to the action of carbon dioxide until the calcium hydroxide has been carbonated. This composition may be dried and molded, or 5 to 16 parts of hexamethylenetetramine may be added prior to molding.

Kendall<sup>21</sup> prepared a liquid mixture of phenol, formaldehyde and water containing dissolved hexamethylenetetramine, in which the formaldehyde is present in sufficient quantity to react with the phenol to form a fusible resin, and the hexamethylenetetramine sufficient to react with the resin to form an infusible product. The mixture is heated to cause reaction and is converted to a fusible resin containing dissolved hexamethylenetetramine but practically no uncombined formaldehyde.

The production of amber-like substances, according to Redman, Weith and Brock,<sup>22</sup> is carried out by first forming an initial product from phenol and formaldehyde without the addition of any condensing agent. Thus, 3 parts of a 40 per cent solution of formaldehyde and 5 parts of phenol are boiled at atmospheric pressure for a period of 60 to 120 hours. A viscous creamy lower layer and a supernatant layer of water practically free from formaldehyde form. Cresol does not require boiling for so long a period, ordinary commercial cresol reacting to

<sup>19</sup> J. W. Aylsworth, U. S. P. 1,020,593, March 19, 1912; *Chem. Abs.*, 1912, 6, 1377. British P. 3,496, 1911; *J.S.C.I.*, 1912, 31, 347. French P. 436,192, 1911; German P. 307,892, 1911.

<sup>20</sup> J. W. Aylsworth, U. S. P. 1,146,299, July 13, 1915; *Chem. Abs.*, 1915, 9, 2432.

<sup>21</sup> D. S. Kendall, U. S. P. 1,418,718, Jan. 6, 1922; *Chem. Abs.*, 1922, 16, 2761.

<sup>22</sup> L. V. Redman, A. J. Weith and F. P. Brock, U. S. P. 1,310,087 and 1,310,088, July 15, 1919; *Chem. Abs.*, 1919, 13, 2429. U. S. P. 1,374,526, April 12, 1921; *J.S.C.I.*, 1919, 38, 647A.

the desired extent in 4 to 12 hours and crude cresol in about 2 hours. With pure phenol the reaction may be accelerated by heating under pressure to 125°C. for 12 to 18 hours. After a viscous resinous mass is made in this manner, 2 additional parts of formaldehyde (that is, 2/3 of the original amount of formaldehyde) are stirred into the first reaction product after removing the water layer which separates in the first stage. This addition is made at a temperature of about 100°C. and the mixture is allowed to cool to 60-70°C. Heat is then applied and water is evaporated rapidly, the temperature rising to about 115°C. Some formaldehyde escapes during this operation. Ordinarily the concentration is carried to a point which renders the mix quite viscous but still permits pouring. Boiling should be stopped before the material reaches a gelatinous state. After this concentration operation 3 to 5 per cent of formaldehyde is added to replace loss and the material is poured into molds, where it is allowed to set at a temperature of 50-100°C. When sufficiently firm it is removed from the molds and kept at the same temperature for a period of several weeks or months, depending on the thickness of the molded masses. By mild heating for a protracted period as described, an amber-like product is obtained which is used to make pipestems, cigar holders and similar articles. A finer color and a harder material which may be machined, sandpapered and buffed to better advantage is obtained by exposure to a finishing heat of 125°C. or higher for several days. The color may be varied by introducing dyes, such as auramin for deep amber or methyl violet for amethyst. Oils or waxes in small quantity yield opaque materials and ground mica or fish-scales produce a shimmering effect when included in the resin.

Glaser<sup>23</sup> utilized the waste liquors or distillates from phenol-formaldehyde manufacture for preparing resins suitable for lacquers by treating them with acids or acid salts below 60°C. After some days the resins precipitate.

Filhol<sup>24</sup> heated phenol and formaldehyde in an alkaline medium (sodium carbonate) at 75-80°C. until the viscosity approached that of the upper limit of polymerization and separated the major portion of the aqueous liquid present. The product was then dehydrated and treated with a catalyst (ethylsulphuric acid or other acid ester) and alcohol, and the polymerization continued at a temperature of 70°C. or lower until the desired stage was reached. Such products may be employed as varnishes. Instead of soluble fusible phenol-formaldehyde resins, acetylated derivatives of these resins, prepared by reaction of acetic anhydride on the resin, may be used. The subsequent action of ethylsulphuric acid produces varnishes and plastic materials having practical advantages because of their transparency, plasticity, luster, and facility of working. The acetylated resins also have the property of plasticizing cellulose acetate, being completely miscible with it in acetone solution. Cost is a drawback to their production.

Walker<sup>25</sup> allowed the condensation of more than 1 mol of formaldehyde with 1 mol of phenol to proceed in the presence of alkaline condensing agents, such as alkali sulphate or caustic alkali, to a stage short of precipitation of the resin, viscosity determinations of the reaction mixture being used for control. The resin is precipitated by the addition of sufficient acid to bring the mother liquor to a pH between 3.2 and 7, the actual acidity and viscosities desired being determined for each specific reaction mixture. Such resins are stated to be particularly light colored, permanent to light and air and, when hardened, of high mechanical strength.

A similar process is described by Schmidt<sup>26</sup> who made a preliminary phenol-

<sup>23</sup> E. Glaser, Austrian P. 106,018, 1921; *Brit. Chem. Abs.* B, 1928, 681.

<sup>24</sup> J. Filhol, U. S. P. 1,505,382, Aug. 19, 1924; *Chem. Abs.*, 1924, 18, 3282.

<sup>25</sup> E. E. Walker, British P. 259,046, 1925; *Chem. Abs.*, 1927, 21, 3276.

<sup>26</sup> F. Schmidt, U. S. P. 1,978,821, Oct. 30, 1934; *Chem. Abs.*, 1935, 29, 252. German P. 608,469, 1935; *Chem. Abs.*, 1935, 29, 2627.



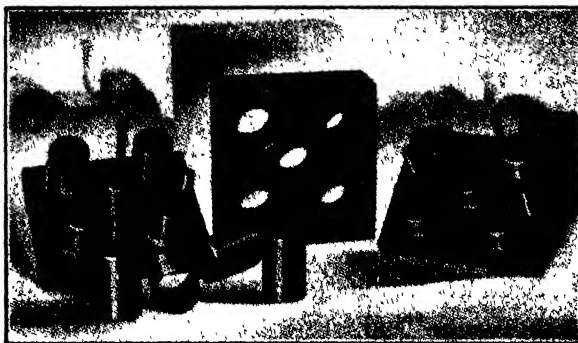
aldehyde condensation in an alkaline medium and then added enough acid (e.g., succinic) to maintain a  $p_H$  of 2.5-5.5. The entire mass was simultaneously kneaded and hardened by heat until a non-sticky plastic mass resulted.

Weith<sup>27</sup> prepared a soluble fusible resin from phenol and formaldehyde by using the approximate ratio of 7.5 phenol groups to 6 methylene groups, particularly with an acid catalyst. This resin is washed with water until the catalyst is removed and is then dehydrated. After determining the precise phenol:methylene ratio, enough phenol is incorporated with the resin to bring this proportion to between 9 and 12 phenols to 6 methylenes. Formaldehyde is then added, to establish a phenol:methylene ratio of 1:1, and also a basic catalyst, e.g., ammonia. The latter may be employed in the form of hexamethylenetetramine or hexamethylenetetraminetriphenol equivalent to about 0.1 per cent by weight of the dry resin. Such a mixture may be hardened by allowing it to stand at 40°C. in a mold until it becomes a firm jelly, removing it from the mold and completing the hardening in heated kilns. This material may be sawed, cut, ground or worked into a variety of forms.

Water-soluble, non-sticking resins were obtained by Hole<sup>28</sup> by boiling 100 parts phenol and 100 parts 40 per cent forma. le in the presence of 25 parts potas-

Fig. 59.  
Molded Phenolic Tubing  
and a Five-Cavity "Over-  
flow" Mold.

Courtesy Bakelite Corporation



sium hydroxide by weight until the desired viscosity is obtained, 30-40 minutes being sufficient to produce a material suitable for most purposes. Cold water is then added (about 72 parts), the product cooled and 2-3 parts of ammonium dichromate and 36 parts of water with sufficient ammonium hydroxide to prevent precipitation are added. Alcohol can be used to decrease the viscosity of the mixture. Other metallic chromates (dissolved, if necessary, in chromic acid) may replace the ammonium salt. Such products may be used in impregnating various materials, for instance, paper pulp to form printing surfaces and matrices,<sup>29</sup> in varnishes and protective coatings and in water-soluble paints which become insoluble on application.

A condensation product which may be shaped in heated molds is made by Menz<sup>30</sup> by boiling phenol and formaldehyde in the presence of both sodium carbonate and sodium bicarbonate and adding acetic acid after boiling to retard the setting. The composition may be colored by dissolving the initial condensed prod-

<sup>27</sup> A. J. Weith, U. S. P. 1,699,727, Jan. 22, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 1294. British P. 323,375, 1928; *Chem. Abs.*, 1930, 24, 3122. French P. 662,495, 1928; *Chem. Abs.*, 1930, 24, 516. German P. 534,808, 1928; *Chem. Abs.*, 1932, 26, 1461.

<sup>28</sup> E. S. Hole, U. S. P. 1,726,151, Aug. 27, 1929; *Chem. Abs.*, 1929, 23, 5019 and U. S. P. 1,799,816, April 7, 1931; *Chem. Abs.*, 1931, 25, 3136. British P. 302,098, 1927; *Chem. Abs.*, 1929, 23, 4357. French P. 663,140, 1929; *Chem. Abs.*, 1930, 24, 698.

<sup>29</sup> E. S. Hole, British P. 278,460, 1926; *Chem. Abs.*, 1928, 22, 2645. See Chapter 22.

<sup>30</sup> H. Menz, British P. 335,194, 1929, to Chemie & Technik J.M.S. Ges.; *Chem. Abs.*, 1931, 25, 1401. See also W. Steffen, French P. 678,250, 1929; *Chem. Abs.*, 1930, 24, 3663.

uct in bone oil or glycerol, adding the coloring matter, and then mixing with another portion of the material to which acetic acid has been added.

Melamid,<sup>31</sup> to form fusible soluble bodies, diluted formaldehyde (60 g. of 30 per cent solution) with an excess of an electrolyte (300-400 g. of 10 per cent sulphuric acid) and added this to phenol (100 g.) at about 40°C. Reaction is complete in 2 hours, after which the excess phenol and water are driven off. The resin melts at about 90°C., is not changed upon being remelted and does not become insoluble.

The solubility, in sodium hydroxide, of the initial condensates of phenol and formaldehyde prepared with alkaline catalysts was utilized by Hiraoka<sup>32</sup> in making a resin for molding. Finely divided resins, softening at 80-90°C., were obtained by adding an excess of water to the sodium hydroxide solutions of the initial condensation products or by neutralizing such solutions with acids. These precipitated resins were converted directly into molding compositions by mixing with wood flour on hot rolls.

Andron<sup>33</sup> made solid resins, partially or entirely convertible to the B state, by dissolving products in the A state in alcoholic alkali, adding benzene, gasoline or other low-boiling solvents and distilling until water and hydrocarbons were removed. In order to produce an odorless phenol-formaldehyde compound, Edwards heats a mixture of 100 gal. cresol, 100 gal. 40 per cent formaldehyde, and 3000 g. caustic soda. Vapors are discharged by an exhaust fan. After a short time a color change occurs, and at this point alcohol is added to arrest the reaction.<sup>34</sup>

**One-Stage Wet Processes.** Processes which are used for making two-stage resins, will, with some slight changes, yield resins of the one-stage type. The principal objection to one-stage operations is the difficulty of securing a uniform product and the minute control which must be exercised. Control of the reaction becomes more and more difficult as water is removed, even though this takes place at low temperature *in vacuo*, and at the end of the dehydration the reaction usually must be promptly checked. In short, the conditions of manufacture must be determined for each specific reaction. The duration of heating is an important factor. Should a batch of one-stage resin show a formaldehyde deficiency, it must be blended with a batch containing an excess, or a calculated amount of additional anhydrous aldehyde has to be added. One-stage resins generally deteriorate in storage more rapidly than the corresponding two-stage resins. Despite these deficiencies, the lower costs of materials will probably make for one-stage resins a more prominent place in the industry.

The essential factor in the preparation of one-stage resins according to McHutchison,<sup>35</sup> is to obtain a compound which contains the requisite amount of formaldehyde for final hardening.<sup>36</sup> This amount is higher in acid than in alkaline condensations. More careful control must be exercised in the manufacture of one-stage resins, because reaction may easily proceed too far and allow the entire charge, which hardens very rapidly once setting has begun, to set in the digester and become too hard to flow out of the bottom outlet, even though pressure is applied.

Six mols of phenol and 7 mols of formaldehyde in condensing with the elimination of 6 mols of water (these being the proportion given by Baekeland<sup>37</sup> for a resin of the saliretin type) would give a yield of resin corresponding to 118

<sup>31</sup> M. Melamid, U. S. P. 1,727,076, Sept. 3, 1929; *Chem. Abs.*, 1929, 23, 5283.

<sup>32</sup> T. Hiraoka, *Proc. World Eng. Congr.*, 1929, 31, 481; *Chem. Abs.*, 1931, 25, 5306.

<sup>33</sup> S. A. Andron, *Russian P.* 23,616, 1931; *Chem. Abs.*, 1932, 26, 2609.

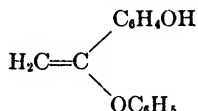
<sup>34</sup> E. S. Edwards, U. S. P. 1,970,649, Aug. 21, 1934, to Panelyte Corp.; *Chem. Abs.*, 1934, 28, 6329.

<sup>35</sup> W. McHutchison, *British Patents*, 1930, 2, 173.

<sup>36</sup> Cf. G. Hugel and M. Vincent, *Chimie et industrie*, 1929, (Feb. Spec. No.), 540. See Chapter 14.

<sup>37</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1909, 1, 159.

per cent of the weight of phenol, as has been shown by Ballandras.<sup>38</sup> Commercial resins show yields as high as 140 per cent of the phenol which may result from incomplete dehydration or from the presence of large quantities of formaldehyde in excess of the specified proportions. If the product is that suggested by Baekeland and Bender<sup>39</sup> as the principal constituent of phenol resinoids of the A stage,



(formed by the condensation of 2 mols of phenol and 2 mols of formaldehyde with the elimination of 2 mols of water) the resin yield would be 113 per cent of the phenol. These quantities of phenol and formaldehyde, according to Baekeland and Bender, are theoretically necessary to produce a resin of the A stage which, by polymerization, will go over to the infusible insoluble resinoid of the C stage. In practice, however, larger quantities of formaldehyde than this are generally used in the manufacture of one-stage resins.

Further addition of formaldehyde to phenol-formaldehyde products reduces their dark color.<sup>40</sup> For example, 110 parts of phenol, 100 parts of 40 per cent formaldehyde solution and 5 parts of sodium carbonate are heated until all the carbon dioxide is given off. From this product 50 to 60 parts of water are distilled *in vacuo* and the dehydrated resin is mixed with 75 parts of potato starch. One hundred parts of the cooled mixture are then heated with 1 part of concentrated hydrochloric acid and 4 additional parts of formaldehyde solution, after which the mass is placed in molds and heated for about 15 minutes at 60°C. The product is washed with dilute sodium carbonate solution.

Pollak and Mohring<sup>41</sup> made infusible, clear, transparent resins by using more than one mol of formaldehyde with one mol of phenol in the presence of a weak organic acid and added, after separating the resin, enough volatile base to pass slightly beyond the point of neutralization. For example, they boiled 100 g. of phenol, 100 g. of formaldehyde (40 per cent commercial) solution, and 1.9 g. of salicylic acid under a reflux until the mixture became creamy, a period of from 10 to 12 hours. They then added 6.5 cc. of dimethylamine solution (153 g. per liter), continued the boiling for another 3 to 5 minutes and washed the resin several times with distilled water. To each 100 grams of resin dehydrated *in vacuo* at 75°C. are added up to 7 cc. of 1 per cent ammonia solution. The product after further dehydration *in vacuo* is hardened at 75-110°C. with or without pressure, and has a specific gravity of about 1.274-1.287.

To make a permanently fusible phenol-formaldehyde resin it has been proposed to heat 7 mols of formaldehyde and 13 mols of phenol in the presence of 5 mols of ammonia (25 per cent solution) and to distil off the ammonia and water.<sup>42</sup> Another method is to form a condensation product with an excess of formaldehyde in a strongly alkaline solution and near the end of the reaction to add enough phenol to bring the total amount to 2 to 5 times the molecular proportion of formaldehyde.<sup>43</sup> If condensation is carried out under reduced pres-

<sup>38</sup> A. Ballandras, *Rev. gen. mat. plastiques*, 1926, 2, 226.

<sup>39</sup> L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, 1925, 17, 225.

<sup>40</sup> British P. 6,430, 1911, to Knoll & Co.; *J.S.C.I.*, 1912, 31, 399. French P. 397,657, (first addn. to), 1911; *J.S.C.I.*, 1911, 30, 1125.

<sup>41</sup> I. Pollak and E. Mohring, U. S. P. 1,475,446, Nov. 27, 1923; *J.S.C.I.*, 1924, 43, 63B.

<sup>42</sup> M. Florenz, U. S. P. 1,982,651, Dec. 4, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1935, 29, 523. British P. 389,099, 1931; *Brit. Chem. Abs.*, B, 1933, 399.

<sup>43</sup> A. Ostersetzer and F. Riesenfeld, U. S. P. 1,892,848, Jan. 3, 1933, to Pollopus, Ltd.; *Chem. Abs.*, 1933, 27, 2259.

sure, the concentration of sodium hydroxide catalyst is increased during the process, because of the evaporation of water.<sup>43</sup>

Bia and de Bielize<sup>44</sup> condensed phenols with a large excess of formaldehyde in the presence of such catalysts as magnesium oxide, sodium carbonate, or a mixture of sodium carbonate and sodium metaborate. The reactants are heated for not more than an hour at the boiling point, cooled to about 50°C., the catalyst neutralized, and the mixture allowed to stand. The liquid resinous product is separated, heated to above 100°C. to dehydrate it and finally molded at 90-112°C. A little paraffin may be added to render the substance more elastic. Either translucent or opaque bodies can be obtained by varying the details of the process.

The reaction between phenol homologues (e.g., cresol) and an excess of formaldehyde (40 per cent solution) was found by Cherry<sup>45</sup> to be catalyzed by slaked lime and aniline (1.5) in an amount equivalent to 6 per cent of the total ingredients. It is stated that this combination of catalysts is especially suited to use with the higher phenolic bodies from the standpoint of rapid hardening, mechanical strength and ease of molding. All the formaldehyde is combined (1.1 mols per mol of phenol) but the product previous to hot-molding is fusible and capable of being worked on mixing rolls.

An opaque resin containing water in colloidal dispersion is obtained by heating phenol (1 mol) with an excess of formaldehyde (2.5 mols) and enough alkali to keep the condensation product in solution. The alkali is neutralized with an acid such as chloroacetic, the salt of which liberates acid during the subsequent heating and the solution is concentrated until it gelatinizes. The gel is hardened by heating at about 80°C.<sup>46</sup>

Hessen<sup>47</sup> refluxed equimolecular quantities of phenol or cresol and formaldehyde in the presence of a basic catalyst until separation into layers occurred. After cooling, the resinous layer is separated from the aqueous layer and one-fifth to one-fourth of the quantity of formaldehyde originally used is added. The resin usually dissolves in this quantity of formaldehyde to a clear liquid. This solution is again heated to separation and the preceding process is repeated 2 to 4 times until the final resin is free from phenol. The proportion of catalyst present in the resin, which decreases with each separation of the aqueous layer, can be maintained by adding fractional parts of the original quantity of the same or other catalyst. The basic substance remaining in the final resin is neutralized, salts formed are removed by extraction with water, and the relatively thin liquid resins obtained are dehydrated. The solid clear final resins are soluble in alcohol, acetone, and sodium hydroxide and may be hardened by heating at temperatures above 60°C. The products, because of their freedom from unreacted phenol, are stated to be stable to light. The quantities used may be as follows:

One hundred parts of phenol, 8 parts of 40 per cent formaldehyde solution, and 1 part of anhydrous sodium carbonate by weight. After removing the aqueous layer, 15 parts by weight of formaldehyde solution are added to the resin and the process is continued as described. The excess base in the compound is neutralized with a 5 per cent tartaric acid solution, the resulting salt is washed out with distilled water, and the resinous solution is evaporated until the desired degree of hardness is reached.

<sup>43</sup> R. Hessen, French P. 763,580, 1934. *Chem. Abs.*, 1934, 28, 5693.

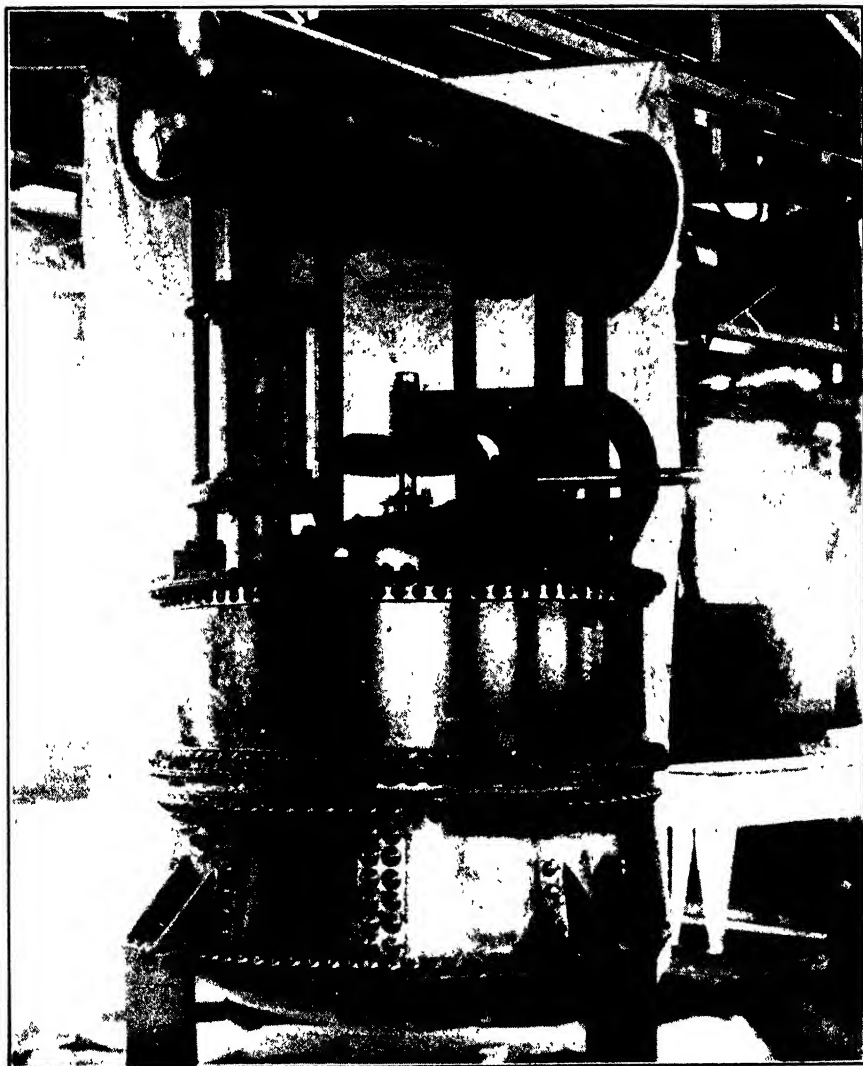
<sup>44</sup> G. Bia and J. de Bielize, French P. 638,387, 1926; *Chem. Abs.*, 1929, 23, 489. British P. 292,629, 1927; *Chem. Abs.*, 1929, 23, 1518. Also M. van Roggen and J. de Bielize, French P. 646,918, 1928; *Chem. Abs.*, 1929, 23, 2257.

<sup>45</sup> O. A. Cherry, U. S. P. 1,994,753, Mar. 19, 1935, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 3073.

<sup>46</sup> F. Pollak and A. Ostersetzer, German P. 569,486, 1927, to Rheinisch-Westfälische, Sprengstoff A.-G.; *Chem. Abs.*, 1933, 27, 2259. A. Ostersetzer and F. Riesenfeld, U. S. P. 1,868,168, May 10, 1932, to Pollopos, Ltd.; *Chem. Abs.*, 1932, 26, 3945. A. Ostersetzer and F. Riesenfeld, German P. 599,990, 1934, to Dynamit-A.-G. vorm. A. Nobel & Co.; *Chem. Abs.*, 1934, 28, 7443.

<sup>47</sup> R. Hessen, U. S. P. 1,816,255, July 23, 1931; *Chem. Abs.*, 1931, 25, 5525. British P. 324,913, 1928; *Chem. Abs.*, 1930, 24, 3914. See also R. Hessen, German P. 601,540, 1934, to Aug. Nowack A.-G.; *Chem. Abs.*, 1934, 28, 7564. British P. 414,435, 1933; *Brit. Chem. Abs. B.*, 1934, 896.

Ostersetzer and Riesenfeld<sup>48</sup> prepared resins free from uncombined phenol and formaldehyde by using protective colloids to keep the resin dispersed throughout



*Courtesy Koven Bros.*

FIG. 60.—Jacketed Steel Mixer with Tubular Condenser.

the liquid in very fine globules. The initial product of the condensation of phenols with aldehydes is a hydrophobe or water-repelling resin and at the moment of its formation it is colloiddally distributed throughout the liquid as an

<sup>48</sup> A. Ostersetzer and F. Riesenfeld, U. S. P. 1,807,545, May 26, 1931; *Chem. Abs.*, 1931, 25, 4096. German P. 516,677, 1928; *Chem. Abs.*, 1931, 25, 3185. Austrian P. 114,871, 1929; *Chem. Abs.*, 1930, 24, 1189. French P. 651,723, 1928; *Chem. Abs.*, 1929, 23, 3589. British P. 238,228, 1927; *Chem. Abs.*, 1929, 23, 678.

emulsion. This emulsion has very little stability and the particles of resin coalesce very quickly to form a coherent resinous substratum with the adsorption of the substances contained in the solution and the occlusion of some of the mother liquor. Purification of this resin by washing is extremely difficult. By keeping it subdivided and dispersed by the action of protective colloids (gum arabic, saponin, tragacanth, dextrin, gelatin, or others) the resin can be hardened by further heating and precipitated as a fine powder. The separate resin particles lose their power of adsorbing substances contained in the solution during the hardening. The following procedure was suggested:

One hundred g. of phenol are boiled under reflux with 110 grams of formaldehyde solution (30 per cent by weight), 150 cc. of 25 per cent sodium chloride solution in which  $2\frac{1}{2}$  g. of gum arabic are dissolved, 50 cc. of 2N sodium hydroxide solution and 25 cc. of 2N ammonia solution. Reaction proceeds with the formation of a milky condensation product and heating is continued until a sand-like precipitation takes place in the hot liquid itself or on the addition of water or acid to a test sample. The powder is separated by filtering after diluting the mixture with water or acid. The resin obtained is of a slightly yellow color, is practically free from all impurities, and can be kept for an indefinite period without changing. Some of the powders are completely soluble in alcohol and alkali.<sup>49</sup> Spitzer<sup>50</sup> proposed to precipitate plastic masses from colloidal solutions of phenol-aldehydes by the addition of a colloid such as urea-formaldehyde hydrosol.<sup>51</sup>

The reaction products of phenol or urea and formaldehyde can be fractionated to obtain resins of varying properties by treating the hot resin with the minimum quantity of water necessary for separation into 2 layers when cooled to 15°C. The aqueous layer can be further separated by repeating the procedure.<sup>52</sup>

Dent<sup>53</sup> used crude phenols in making resins for hot molding. He states that previous attempts with such raw materials failed because of difficulties arising on attempted dehydration. This he avoided by neutralizing the basic catalyst with an acid that leaves an insoluble residue in the mass. After this he added formaldehyde and ammonia to form hexamethylenetetramine to act as the catalyst for the final setting. He further stated that as this catalyst has little or no action below 100°C., the resin so made can be dried by heat and vacuum without risk of setting.

**Dry Processes.** One-stage and two-stage dry processes can be differentiated in the same way as the wet processes. Their use is practically limited, as mentioned before, to the production of material to be machine-turned or cast. The products are light-colored, and transparent, translucent or opalescent for such uses as substitutes for amber or tortoise shell. Dry operations are not usually applied at present to the preparation of fusible soluble resins. If a dry process is used it is generally carried out in one stage, directly to infusible insoluble resins, although it can be taken only to the stage of soluble fusible resins. If fusible soluble resins prepared by a wet process are hardened by addition of anhydrous aldehyde, although this second stage is really a dry operation, the entire method is considered a two-stage wet process.

The aldehyde commercially useful in dry processes is limited practically to paraformaldehyde as such or as hexamethylenetetramine.<sup>54</sup> Other anhydrous aldehydes, such as gaseous formaldehyde, various formaldehyde polymers, (trioxy-

<sup>49</sup> See also A. Bresser, *British Plastics*, 1932, 4, 105, 112; *Brit. Chem. Abs.* B, 1932, 947.

<sup>50</sup> A. Spitzer, Swiss P. 153,843, 1931; *Chem. Abs.*, 1933, 27, 1113.

<sup>51</sup> See also A. A. Poulverel, French P. 662,227, 1928; *Chem. Abs.*, 1930, 24, 476.

<sup>52</sup> I. Femmann, British P. 397,909, 1933; *Brit. Chem. Abs.* B, 1933, 929. French P. 752,431, 1933; *Chem. Abs.*, 1934, 28, 1208.

<sup>53</sup> H. M. Dent, U. S. P. 1,894,088, Jan. 10, 1933, to General Plastics, Inc.; *Chem. Abs.*, 1933, 27, 2259.

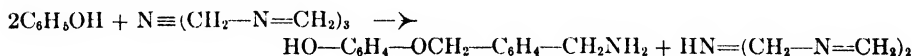
<sup>54</sup> Strictly speaking the reaction between phenol and paraformaldehyde is not a dry process since it liberates water, but this classification into wet and dry grew out of controversies and has been continued in the industry.

methylene or metaformaldehyde, for instance) and acetaldehyde polymers (paraaldehyde and metaldehyde) have found no extensive application.

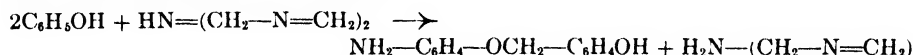
*Processes Using Hexamethylenetetramine.* In the dry state, hexamethylenetetramine<sup>55</sup> represents a rather costly material for the preparation of initial or fusible resins. More frequently, as may be expected, it is employed in small proportion as a finishing or hardening agent. As Baekeland indicated,<sup>56</sup> a fusible resin transformable by heat to an infusible body requires an added proportion of formaldehyde in its making, approximately 7 mols of formaldehyde to 6 mols of phenol being necessary. This amount of course may be supplied all at once or in two or more stages. Making fusible resins with the aid of one catalyst and transforming to an infusible resin in the presence of another catalyst constitutes the basis of scores of processes differing but slightly in details. That hexamethylenetetramine should be repeatedly advocated in such duplex processes is not surprising in view of its well known properties.<sup>57</sup>

Redman, Weith and Brock<sup>58</sup> considered the reaction between hexamethylenetetramine and phenol in aqueous solution to be substantially different from that progressing when the reagents are heated in a dry state. The simplest product which forms when phenol reacts with hexamethylenetetramine is the crystalline compound, hexamethylenetetraminetriphenol.<sup>59</sup> However, when 1 mol of hexamethylenetetramine and 6 mols of phenol are boiled in aqueous solution, a light yellow transparent viscous liquid separates which on continued heating increases in viscosity. At room temperature it becomes a brittle amber-like solid.

Lebach<sup>60</sup> stated that hexamethylenetetraminetriphenol, when heated in the dry state, evolves ammonia and yields an insoluble and infusible substance. Lebach considered this product to be Bakelite but this was challenged by Redman, who looked upon Bakelite as a material in which 6 phenols are united with 7 methylene groups. As hexamethylenetetraminetriphenol has a composition of 6 phenols for every 12 methylene groups, over 40 per cent more methylene is present than is required, according to Redman, to produce Bakelite. When hexamethylenetetraminetriphenol is heated, besides ammonia there is evolved a substance having an odor somewhat resembling methylamine. The latter by-product is not present when the phenol is increased to 6 mols of phenol for 7 methylenes. If, however, dry hexamethylenetetramine and anhydrous phenol are mixed and the mixture heated to 60°C or higher, a reaction begins with the evolution of ammonia which, according to Redman's investigation, is the only by-product. With phenol in excess and if the mixture is heated to the boiling point, the reaction proceeds with great rapidity. Nearly all the ammonia is evolved in the first 10 minutes of boiling. Representing the formula of hexamethylenetetramine<sup>61</sup> as  $N\equiv(CH_2-N=CH_2)_3$ , this reaction may take place



and a second reaction may occur:



<sup>55</sup> This substance, also called *formin*, but more commonly by the abbreviation "*hexa*," always forms when ammonia and formaldehyde are mixed. Therefore, when ammonia is added for catalytic purposes to a mixture of phenol and formaldehyde, hexamethylenetetramine is produced. See Chapter 16.

<sup>56</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1909, 1, 135.

<sup>57</sup> A discussion of the effect of pH on the dissociation of hexamethylenetetramine and hexamethylenetetramine-ethanol hydride is given by G. Toussaint, J. Detrie and M. Veram, *Compt. rend. soc. biol.*, 1934, 117, 191; *Chem. Abs.*, 1935, 29, 727.

<sup>58</sup> L. V. Redman, A. J. Weith and F. B. Brock, *Ind. Eng. Chem.*, 1914, 6, 3.

<sup>59</sup> H. Moschatos and B. Tollens, *Ann.*, 1893, 272, 280.

<sup>60</sup> H. Lebach, *Z. angew. Chem.*, 1909, 22, 1600.

<sup>61</sup> L. V. Redman, A. J. Weith and F. B. Brock, *Ind. Eng. Chem.*, 1914, 6, 3.

This continues until all the  $\text{CH}_2$  groups have combined with the phenol and ammonia remains as the by-product. The intermediate product aminosaligeno-saligenin has been isolated.

Heating a mixture of hexamethylenetetramine and an excess of phenol produces soluble and fusible resins (Novolak).<sup>42</sup> These are soluble in alcohol, acetone, and aqueous caustic alkali. The resin remains a liquid at temperatures up to  $180^\circ\text{C}$ . and even after being subjected to this temperature for many hours. When cold it hardens to a glassy material which is more brittle than common rosin. If the phenol is decreased below the ratio of 12 mols to 1 mol of hexamethylenetetramine, the liquid thickens and the resin changes to an infusible and insoluble transparent substance of yellow or red color. Nine mols of phenol to 1 mol of hexamethylenetetramine yield a complex which is quite brittle in the cold but rubbery when heated to  $170^\circ\text{C}$ . Eight mols of phenol to 1 of hexamethylenetetramine is brittle in the cold and when hot resembles gelatinized tung oil. As the phenol is reduced the reaction product becomes less elastic when hot and in the ratio of about 5 mols of phenol to 1 of hexamethylenetetramine is quite hard at all temperatures. At room temperature this is a dense tough product, the tensile strength of which ranges from 4000 to 5200 pounds per square inch. Decreasing the phenol below 5 or 5.5 mols to 1 of hexamethylenetetramine makes the resin brittle on account of the presence of an excess of crystalline hexamethylenetetraminetriphenol.

A mixture of phenol (6 mols) and hexamethylenetetramine (1 mol) on heating strongly, for example at  $180^\circ\text{C}$ ., evolves ammonia rapidly and produces a spongy material. This may be ground readily and when pressed in hot molds at 4 to 6 tons per square inch yields a homogeneous transparent solid article, of good mechanical strength and high dielectric properties, which is quite inert to reagents. If the same composition is heated on a water bath for 25 hours, less than half of the total ammonia is evolved and the mass is viscous when hot and brittle when cold. Redman succeeded in casting in open molds mixtures made in these proportions, allowing hardening to take place by heating without application of external pressure. Transparent rods 2 feet long and  $1\frac{1}{2}$  inches in diameter free from fractures and gas bubbles were obtained.

Aylsworth<sup>43</sup> utilized organic acid anhydrides, such as benzoic or phthalic anhydride, to absorb or fix the ammonia liberated during the final reaction when hexamethylenetetramine is used. In addition to absorbing ammonia by forming amides, these anhydrides were stated to be valuable in toughening the resin. Anhydrides of some acids also combine with water and thus remove any water liberated during the reaction. Higher members of the acetic acid series, for example, stearic anhydride, have also been used by Aylsworth.

Baekeland<sup>44</sup> prepared amber-like products by heating phenol and hexamethylenetetramine, with or without water, to form hard, infusible resins containing free ammonia.

The reaction between phenol and hexamethylenetetramine was carried out under anhydrous conditions by Goldsmith<sup>45</sup>. The proportions of the ingredients are such that one phenolic group is introduced to each methylene group. The mixture is heated, with the evolution of ammonia, until a sample solidifies on cooling. The product is soluble in ordinary solvents but can be hardened and made infusible and insoluble by further heating under pressure. The employment of a solvent facilitates control of the reaction and produces a more homo-

<sup>42</sup> L. V. Redman, A. J. Weith and F. P. Brock, *loc. cit.*

<sup>43</sup> J. W. Aylsworth, U. S. P. 1,020,594, Mar. 19, 1912; *J.S.C.I.*, 1912, 31, 339A. U. S. P. 1,046,420, Dec. 3, 1912; *J.S.C.I.*, 1913, 32, 35. U. S. P. 1,102,634, July 7, 1914; *J.S.C.I.*, 1914, 33, 931.

<sup>44</sup> L. H. Baekeland, U. S. P. 1,187,230, June 13, 1916; *Chem. Abs.*, 1916, 10, 2031.

<sup>45</sup> B. B. Goldsmith, U. S. P. 1,230,829, June 19, 1917; *Chem. Abs.*, 1917, 11, 2283.



geneous resin. Goldsmith<sup>66</sup> used xylene as a solvent to moderate the reaction. If the amount of xylene is large, the resin separates during the latter part of the process either as a solid mass or as a pulverulent precipitate. For example, 40 g. of phenol, 10 g. of hexamethylenetetramine and 50 g. of xylene are heated together under a reflux condenser, the temperature being slowly raised to about 165°C. when the product precipitates as a resinous mass and the xylene can be poured off and used again. Redman<sup>67</sup> heated 1 mol of hexamethylenetetramine with more than 5 mols of phenol in the presence of a solvent such as alcohol or acetone, which acts as a controlling agent and retards the reaction. After about 5 hours at 80° an initial condensation product can be used as a coating or binder, glue or adhesive. By subjecting it to further heat and pressure the material is transformed into a hard, infusible, insoluble resin. Glycerol can be added to the raw materials to make the final product more pliable and to produce a ruby-red color.

The substitution of hexamethylenetetramine, according to Redman, Weith and Brock,<sup>68</sup> overcomes a number of the difficulties which arise when aqueous formaldehyde is used. A molding composition may be prepared from 75 parts of hexamethylenetetramine dissolved in 300 parts of cresol and mixed with 600 parts of asbestos pulp and 150 parts of asbestos fiber. Pitch, asphalt or varnish resins may be added. The composition is molded by hot pressing to yield infusible articles. Hydrobenzamide or benzaldehydeamine may also be used with phenol, cresol or xlenols.

From phenol or cresol and hexamethylenetetramine Redman<sup>69</sup> made soluble fusible resins which could be treated with formaldehyde or more hexamethylene-tetramine to form hard, infusible, insoluble bodies. The mixture is in the proportion of 11 mols of phenol or 10 mols of cresol to 1 mol of hexamethylenetetramine. Thus, 103 pounds of phenol and 14 pounds of hexamethylenetetramine are heated to a temperature of 130°C., at which point reaction takes place with the evolution of heat. The temperature rises to 180°C. and ammonia is evolved. When ammonia ceases to come off heat is applied and the reaction product is boiled at a temperature of approximately 183°C. for a period long enough to eliminate most of the nitrogen (usually 5 hours). According to Redman, the resinous material consists of about 38 per cent of phenol and 62 per cent of phenyl-endekasaligeno-saligenin,  $C_6H_5(OCH_2C_6H_4)_{11}OCH_2C_6H_4OH$ . To prepare an infusible resin the batch is allowed to cool to about 105°C. and 15 pounds of actual formaldehyde (in the form of 40 per cent solution) and about one-half pound of hexamethylenetetramine are added. The mass is further cooled to a temperature of 65-75°C. and is held at this temperature until hardening takes place. When cresol is used, 1080 pounds of it and 140 pounds of hexamethylenetetramine are heated to 140°C. and the temperature is allowed to rise spontaneously while ammonia is being evolved. When the evolution of ammonia ceases, heat is applied and the batch is maintained at a temperature of 165°C. for 48 hours. A portion of the free cresol (as much as 10 to 30 per cent of that originally used) is eliminated by blowing hot air through the fused mass. Then 78 pounds of creosote oil are added at a temperature between 85° and 125°C., and 120 pounds of hexamethylenetetramine are introduced, together with small amounts of dyes, pigments, fats or waxes. This material is mixed with fillers by treating on milling rolls to form a sheeted product which is ground to a powder for molding.

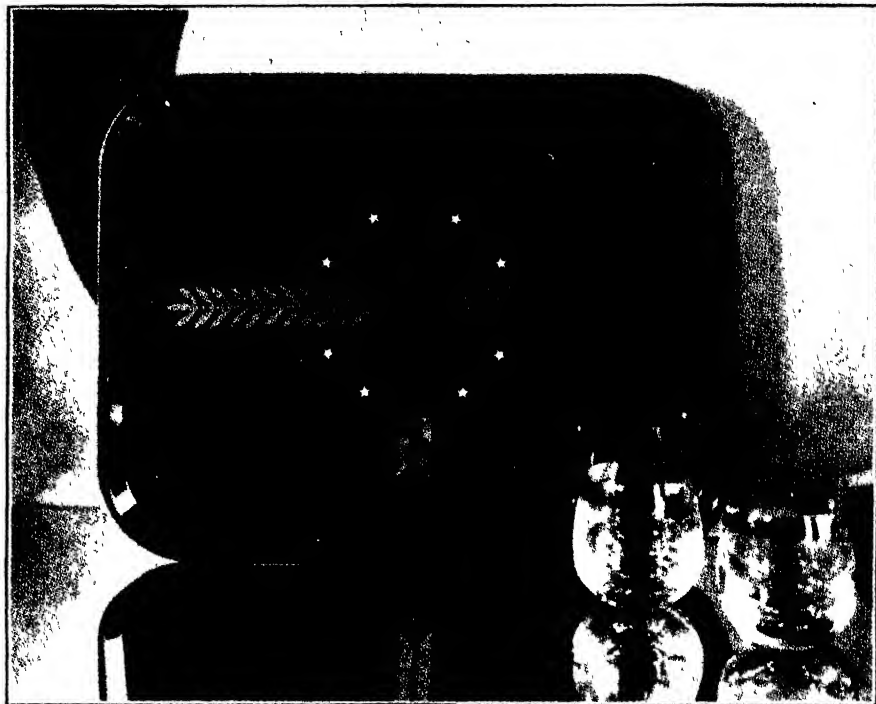
<sup>66</sup> B. B. Goldsmith, U. S. P. 1,375,959, Apr. 26, 1921; *Chem. Abs.*, 1921, 15, 2733.

<sup>67</sup> L. V. Redman, U. S. P. 1,107,703, Aug. 18, 1914; *Chem. Abs.*, 1914, 8, 3377.

<sup>68</sup> L. V. Redman, A. J. Weith and F. P. Brock, U. S. P. 1,368,753, Feb. 15, 1921; *Chem. Abs.*, 1921, 15, 1196.

<sup>69</sup> L. V. Redman, U. S. P. 1,188,014, June 20, 1916; *Chem. Abs.*, 1916, 10, 2131. U. S. P. 1,242,592, Oct. 9, 1917; *Chem. Abs.*, 1918, 12, 209.

**Use of Polymers of Formaldehyde.** Aylsworth<sup>70</sup> heated a formaldehyde compound (having the formula  $[\text{CH}_2\text{O}]_n$ , in which  $n$  is less than 4) at a temperature not exceeding  $180^\circ\text{C}$ . with an anhydrous fusible phenol resin for a length of time sufficient to cause complete hardening. The proportions of the two reacting bodies are determined by ascertaining the amount of free phenol in the phenol resin and calculating the amount of formaldehyde compound necessary for complete combination to form a hard infusible resin.



*Courtesy Bakelite Corp.*

FIG. 61.—Micarta Serving Tray with Inlaid Metal Design.

The production of light-colored phenol-formaldehyde resins depends, according to Pollak, on the use of a minimum amount of condensing agent and the removal of excess phenol by washing with warm water. The use of a sensitive form of trioxymethylene ( $\beta$ - and  $\gamma$ -polyoxymethylene) makes the addition of a special catalyst unnecessary. A method employed by Pollak<sup>71</sup> consists in adding anhydrous trioxymethylene (20 parts) to phenol (370 parts) and metacresol (6 parts) heated on a water bath. Reaction begins at  $85^\circ\text{C}$ . with the evolution of heat and the temperature rises to above  $100^\circ\text{C}$ . After the temperature has fallen below  $100^\circ$  additional trioxymethylene is added and the heating and cooling allowed to take place after each addition until 80 parts of the methylene compound have been introduced. The mass is repeatedly washed with large quantities of water at a temperature below  $40^\circ\text{C}$ . and is then heated to about  $130^\circ\text{C}$ . The resin is used as a substitute

<sup>70</sup> J. W. Aylsworth, U. S. P. 1,102,630, July 7, 1914; *J.S.C.I.*, 1914, 33, 931.

<sup>71</sup> F. Pollak, U. S. P. 1,210,982, Jan. 2, 1917; *Chem. Abs.*, 1917, 11, 710.

for shellac. Discoloration of the resin on exposure to light and air is considered by Pollak<sup>72</sup> to be caused by the presence of small amounts of leuco bases, which gradually oxidize to colored substances. These may be washed out of the resin along with free phenol. A soft resin, therefore, is prepared and very thoroughly washed first with water and then with water containing methyl alcohol or acetone.

In one instance, Pollak heated 100 parts by weight of crystallized phenol with 80 parts of 40 per cent aqueous formaldehyde in the presence of 0.2 part of sodium phenolate. The heating is carried out under reflux until the condensation product precipitates. The heavier resinous layer is separated from the supernatant aqueous solution and is washed repeatedly with water, followed by water containing 10 per cent of methyl alcohol and finally by cold water. The residue is freed from the last traces of phenol by distillation *in vacuo*. When heated in molds at 95-120°C., the infusible and insoluble product is transparent, of a light yellow color and is stated to be air- and light-proof. In another case Pollak treated 94 parts of crystallized phenol with 15 parts of finely powdered  $\alpha$ -polyoxymethylene and added enough 1/5 *N* sulphuric acid to start an exothermic reaction and to dissolve the polyoxymethylene. The mixture is heated to about 85°C., 5 additional parts of polyoxymethylene and a further quantity of the sulphuric acid solution being added after the reaction has started. The soft resinous mass is washed repeatedly with water and treated with a 0.3 per cent solution of hydrogen peroxide. After standing for some hours the resin is further washed with water. This material is an intermediate which when mixed with fresh formaldehyde or polyoxymethylene can be converted into a light- and air-proof insoluble product.<sup>73</sup>

If phenol or cresol is heated with an excess of paraformaldehyde in the absence of a catalyst (1 mol of phenol to 1½ mols of paraform) an oily liquid is formed, which becomes solid at a high temperature.<sup>74</sup> When this liquid condensation product is mixed with a soluble fusible phenol-formaldehyde resin in the presence of acid or alkaline catalysts and heated, the final products are insoluble and infusible, although soluble intermediates may be obtained.<sup>75</sup> Snelling,<sup>76</sup> in a somewhat similar manner, prepared one intermediate substance from a phenol and hexamethylenetetramine and a second from a phenol and an anhydrous polymerized aldehyde. These two products were then mixed in such proportions that the excess of ammonia in the first compensated for the deficiency in the second.

A process proposed by Morgan and Drummond<sup>77</sup> consists of heating a mixture of a phenol, a solid polymer of formaldehyde, a catalyst such as lime or hydrochloric acid, and an inert organic solvent. The resin solution produced is neutralized and washed, preferably with saturated sodium thiosulphate solution, and dried.

Another form of anhydrous aldehyde, namely, gaseous formaldehyde, was used by Aylsworth.<sup>78</sup> Formaldehyde gas is introduced with agitation into an autoclave containing phenol or cresol held at a temperature of 125-170°C. Pressure is maintained slightly in excess of the vapor tension of the mixture by feeding the compressed gas into the autoclave as rapidly as it combines with the phenol. At 50-100 pounds per square inch very good results are obtained. The operation is continued until a sample shows 12 per cent or less of free phenol. The resulting resinous product is dehydrated at 205°C. and is cast into slabs for subsequent use. Aylsworth<sup>79</sup> produced molded articles by placing phenol in a heated mold and resinifying it by introducing gaseous formaldehyde under pressure.

<sup>72</sup> F. Pollak, U. S. P. 1,211,227, Jan. 2, 1917; *Chem. Abs.*, 1917, 11, 693. U. S. P. 1,369,352, Feb. 22, 1921; *Chem. Abs.*, 1921, 15, 1381.

<sup>73</sup> F. Pollak, British P. 13,281, 1912; *Chem. Abs.*, 1914, 8, 434. British P. 20,977, 1914; *J.S.C.I.*, 1915, 34, 1154. British P. 14,490, 1915; *J.S.C.I.*, 1916, 35, 1226. (Swiss P. 73,579, 1916; *Chem. Abs.*, 1917, 11, 877. Swedish P. 41,638, 1916; *Chem. Abs.*, 1917, 11, 2050.)

<sup>74</sup> German P. 475,865, 1918, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1929, 23, 3782.

<sup>75</sup> German P. 484,046, 1920, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1930, 24, 1236.

<sup>76</sup> W. O. Snelling, U. S. P. 1,462,771, July 24, 1923; *Chem. Abs.*, 1923, 17, 3076.

<sup>77</sup> G. T. Morgan and A. A. Drummond, British P. 315,442, 1928; *Brit. Chem. Abs. B*, 1928, 863.

<sup>78</sup> J. W. Aylsworth, U. S. P. 1,029,737, June 18, 1912; *Chem. Abs.*, 1912, 6, 2547.

<sup>79</sup> J. W. Aylsworth, U. S. P. 1,033,044, July 16, 1912; *Chem. Abs.*, 1912, 6, 2696.

## PHENOL-ALCOHOL RESINS

The phenol alcohols (see Chapter 14), such as saligenin or hydroxybenzyl alcohol, as well as dihydroxydiphenylmethanes, have been shown to serve as intermediates in the formation of phenol-formaldehyde condensation products. These materials, being crystalline, offer themselves readily to purification. Other crystalline intermediates, such as those obtained from condensation of acetone and phenol, which can also be used for the preparation of resins, are described in Chapter 18.

Methods of forming phenol alcohols from phenol and formaldehyde have been described by Manasse,<sup>80</sup> Lederer,<sup>81</sup> and Granger,<sup>82</sup> as already mentioned.<sup>83</sup>

Infusible molded articles were made by Baekeland<sup>84</sup> from hydroxybenzyl alcohol or other phenol alcohols. In one case phenol alcohols or their anhydrides (sahretins) and formaldehyde, with or without a condensing agent, are heated to give hard thermo-rigid resins. In place of formaldehyde, its polymers may be used. When ammonia is employed as a condensing agent hexamethylenetetramine is produced which of course serves as a hardening agent. In the infusible state the resin may be incorporated with a variety of filling materials (asbestos, wood fiber, mineral powders and pigments) in the same manner as is employed in making rubber compositions. Organic substances such as naphthalene, anthracene, aniline, phenols, pitch, asphaltum, cumarone resins and other resinous bodies and paraffin may be added. Another procedure is that of treating phenol alcohols or their anhydrides with basic catalysts to yield resinous substances which are less hard and less resistant to heat and to solvents than the products obtained above with the aid of additional formaldehyde. Appropriate catalysts are ammonia or its carbonate, caustic alkalies or their carbonates, aniline, pyridine, barium or calcium hydroxides, alkali sulphides, acetates and cyanides, borax, soaps and trisodium phosphate. Fillers may be incorporated with the resinous material thus obtained and the composition molded under heat and pressure.

Aylsworth<sup>85</sup> prepared phenol alcohols by reacting phenol and formaldehyde in the presence of an alkaline solution such as milk of lime. The product is mixed with fillers, with or without the addition of hexamethylenetetramine, and is treated with an acid to neutralize the alkali. The resultant composition is dried and is then available for molding. The process also is adapted for preparing varnishes and lacquers.

Amann and Fonrobert<sup>86</sup> prepared definite phenol alcohols, free from resinous and other by-products, by slowly adding a mono- or dicyclic phenol (phenol, cresol, naphthol or dihydroxydiphenylpropane), particularly in alkaline solution, to a quantity of aldehyde at least equal to the theoretical amount that can combine with the phenol. The oily product can be converted into infusible bodies under heat and pressure by treating them with further quantities of formaldehyde.<sup>87</sup> Baekeland<sup>88</sup> obtained a soluble composition (which could be rendered insoluble

<sup>80</sup> O. Manasse, *Ber.*, 1894, 27, 2409; U. S. P. 526,786, Oct. 2, 1894. See also German P. 85,588, 1894, to F. Bayer & Co.; *Chem. Zentr.*, 1896, 1, 1120.

<sup>81</sup> L. Lederer, *J. prakt. Chem.*, 1894, 50, (2), 224.

<sup>82</sup> F. S. Granger, *Ind. Eng. Chem.*, 1932, 24, 442.

<sup>83</sup> See Chapter 13.

<sup>84</sup> L. H. Baekeland, U. S. P. 1,038,475, Sept. 10, 1912; *Chem. Abs.*, 1912, 8, 3534. U. S. P. 1,146,045, July 13, 1915; *Chem. Abs.*, 1915, 9, 2432. U. S. P. 1,187,232, June 13, 1916; *Chem. Abs.*, 1916, 10, 2031.

<sup>85</sup> J. W. Aylsworth, U. S. P. 1,111,288, Sept. 22, 1914; *Chem. Abs.*, 1914, 8, 3634.

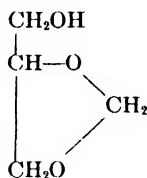
<sup>86</sup> A. Amann and E. Fonrobert, U. S. P. 1,614,171, Jan. 11, 1927, to Chem. Fabr. K. Albert G.m.b.H.; *British P.* 261,472, 1925; *Brit. Chem. Abs.* (B), 1927, 119. German P. 536,171, 1923; *Chem. Abs.*, 1932, 26, 1077.

<sup>87</sup> A. Amann and E. Fonrobert, U. S. P. 1,614,172, Jan. 11, 1927, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1927, 21, 805.

<sup>88</sup> L. H. Baekeland, U. S. P. 1,442,420, Jan. 16, 1923; *Chem. Abs.*, 1923, 17, 1031.

by further heating) from hexamethylenetetraminetriphenol and a phenol alcohol, for instance, hydroxybenzyl alcohol.

Sutherland<sup>90</sup> heated hydroxybenzyl alcohols, hydroxy  $\beta$ -naphthol alcohols or trihydroxybenzyl alcohols, at about 100°C. with the cyclic ether of a polyhydric alcohol in the presence of an acid or alkaline condensing agent to produce infusible products. Cyclic ethers of polyhydric alcohols proposed are formalglycerol, formalglycol, acetalglycerol and benzalglycol. Catalysts suggested include formic, hydrochloric and phosphoric acids and sodium hydroxide, calcium hydroxide and sodium carbonate. Thus, 50 parts of o-hydroxybenzyl alcohol, 50 parts of formalglycerol,



and 3.5 parts of 30 per cent ammonium hydroxide are heated at 70°C. for 2 to 3 hours and then poured into an open vessel, the temperature being gradually raised to 100°C. When the product becomes solid, the temperature is increased rapidly to about 125°C. and maintained until the mass is fully cured. The product is a light yellow transparent, semi-rigid, amber-like solid, very flexible when heated, infusible, insoluble in all ordinary solvents, highly resistant to acids and many alkalis, and possesses high dielectric properties.

Kulas and Pauling<sup>91</sup> prepared phenol-aldehyde resinous condensation products by condensing methylenephenols and phenol alcohols. A methylene-diphenol mixture is prepared by the action of an acid such as hydrochloric acid on a phenol and formaldehyde; phenol alcohols are formed by the action of a basic condensing agent upon an additional mixture of phenol and formaldehyde. As an instance, 50 parts of cresol are heated with 25 parts of 40 per cent formaldehyde and 1 to 1.5 parts of moderately concentrated hydrochloric acid to the point where separation begins, then 100 parts of cresol, 75 parts of 40 per cent formaldehyde and 20 to 25 parts of aqueous ammonia (25 per cent) are added. The mixture is boiled for a considerable time and then dehydrated to obtain a soluble transparent resin. By gradually heating the soluble body thus prepared it can be transformed into an insoluble form.

If the reaction between formaldehyde and an alkali phenolate is carried out at low temperatures, the amount of formaldehyde undergoing the Cannizzaro reaction (see Chapter 14), as compared with the amount entering into the condensation, is substantially lessened. Accordingly, it is desirable to keep the reaction mixture cold until all of the formaldehyde becomes bound.<sup>92</sup>

Polyalcohols of phenols, formed by using an increased proportion of formaldehyde in alkaline condensation with phenols, are converted into pale acetone-soluble resins by the addition of strong acids. These resins are said to have superior curing properties and to withstand the effects of light both before and after the cure.<sup>93</sup>

<sup>90</sup> L. T. Sutherland, U. S. P. 1,523,459, Jan. 20, 1925, to Carboloid Products Corp.; *Chem. Abs.*, 1925, 19, 1760.

<sup>91</sup> C. Kulas and C. Pauling, U. S. P. 1,609,367, Dec. 7, 1926; *Chem. Abs.*, 1927, 21, 333. German P. 431,619, 1922; Canadian P. 240,145, 1923. Swiss P. 106,557, 1923; *Brit. Chem. Abs.*, B, 1926, 890.

<sup>92</sup> F. S. Granger, U. S. P. 1,946,459, Feb. 6, 1934, to Combustion Utilities Corp.; *Chem. Abs.*, 1934, 28, 2556.

<sup>93</sup> F. S. Granger, U. S. P. 1,956,530, Apr. 24, 1934; *Chem. Abs.*, 1934, 28, 4256.

## CONTINUOUS PROCESSES

The advantages of continuous processes are at once apparent. In large digestors very careful control of the reaction is necessary, and an accident to the water-cooling system, for instance, might mean the loss of the entire large batch due to the uncontrolled heat of combination converting the mass to the infusible state. In a continuous system where reaction is confined to small quantities of material such loss would be relatively small. The more careful control of a continuous operation and its higher production rate are special advantages. The exothermic reaction of condensation can also be made to preheat the fresh reaction mixture.

Turkington<sup>93</sup> proposed to mix the phenol, formaldehyde solution and catalyst and to pump the mixture continuously through heated reaction coils. A steam piston pump capable of producing a pressure of a few hundred pounds per square inch is used and the pressure is maintained by an adjustable pressure regulator.

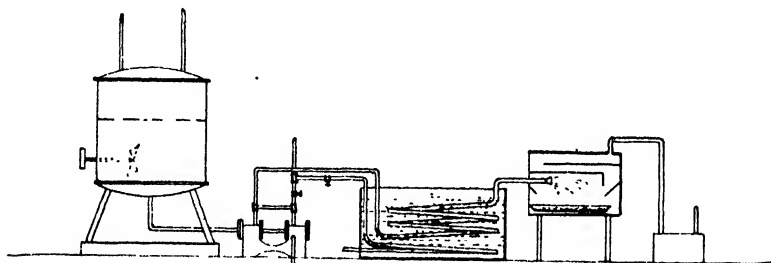


Fig. 62.—Continuous Process for the Production of Phenol-Formaldehyde Resins. (V. Turkington.)

From the pump the mixture passes through a reaction coil, formed of extra heavy iron or copper tubing immersed in an oil bath. The bath is heated by a closed steam coil supplied with steam at about 125 pounds pressure to initiate the reaction. The coil may also be supplied with water connections for cooling, should this be required. The reaction is exothermic and the heat of reaction ordinarily suffices to maintain the proper temperature of the oil bath.

The reaction mixture is forced slowly through the heating coil, where the flow and bath temperature are regulated to complete the reaction to the desired point before the mixture passes the discharge end of the coil. The rate of flow will depend largely on the length of this coil. On passing from the coil the reaction mixture is a fluid material containing a large proportion of water. This mixture is dehydrated by spraying into a chamber in which a relatively high vacuum is maintained. The resin is then cooled to 50°C. or lower which prevents further reaction. See Figure 62.

Another continuous process consists in introducing the reactants into a preheater (a heated copper coil) and atomizing the mixture or distributing the reaction product upon rollers or endless belts during the heating with or without a previous passage through a water separator. The finished resin may be used as it leaves the concentration plant, for example by passing it directly to a paper-sizing machine.<sup>94</sup>

<sup>93</sup> V. H. Turkington, U. S. P. 1,660,403, Feb. 28, 1928, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 1486.

<sup>94</sup> C. Kulas and J. Scheiber, British P. 230,861, 1925; *J.S.C.I.*, 1925, 44, 890B. German P. 436,779, 1924.

Hoskins<sup>96</sup> suggested a process utilizing a silent electrical discharge in which phenol and formaldehyde are vaporized in two separate stills and passed into a tubular treating conduit surrounded by a hot-water jacket. The conduit itself is one electrode and surrounds the other of a high-voltage electric circuit. In this way the mixed reagents in the vapor state are subjected to a silent electric discharge. The vapors are condensed on emerging from the conduit, and the condensate is heated to evaporate phenol and formaldehyde. About 40 per cent of the original material remains as a clear, brown, brittle resin, soluble in alcohol and ether mixtures but only slightly soluble in alcohol alone. The process is best carried out at reduced pressure. The resin on heating at 280°C. or above for any appreciable length of time becomes insoluble.

#### PURIFICATION OF RESINS

The questions of the action of light and air on phenol-formaldehyde resins and resinoids and of purification processes to minimize this have received much consideration. It is well known that exposure to light often has a darkening effect whether these resins are in the form of coatings, moldings or fabricated resinoids.

One explanation for the darkening is that it is caused by free phenol. Pollak<sup>98</sup> on the other hand laid it to the presence of small amounts of leuco bases which gradually oxidize to colored substances.<sup>97</sup> Pollak<sup>98</sup> used acid catalysts and found the amount of acid to be the controlling factor of color in the finished resin. When the quantity of acid used is less than 1-2 per cent of the end product perfectly white or slightly brownish or yellowish products result. However, in considering the causes of the dark color assumed by novolaks, Mashkilleison and Zimmerman<sup>99</sup> concluded that neither the presence of free phenol (up to 4 per cent) in the finished product, nor the purity of the phenol, nor the amount of catalyst is of importance. In all cases studied by them there was a considerable change in the original color after 30 days' exposure to light. The nature of the catalyst to a large extent influences both the original color and its stability. From the standpoint of color permanence, best results are obtained with weak mineral acids. Strong mineral acids and organic acids give poorer results and the least satisfactory are the metallic salts of mineral acids.

Redman, Weith and Brock<sup>100</sup> found that even the brightest light does not affect a phenol resinoid that is kept out of contact with oxygen. They observed that non-oxidizing gases (carbon dioxide, methane and ordinary illuminating gas) or the absence of air (vacuum) tend to prevent darkening even if the sample is placed in direct sunlight. Such methods for preventing darkening are far from practical, and various others have been proposed, as previously mentioned, for removal of the substances which cause darkening. Pollak<sup>101</sup> suggested washing the resin with warm water; Hessen<sup>102</sup> treated the liquid resin with additional formalde-

<sup>96</sup> W. Hoskins, U. S. P. 1,473,347, Nov. 6, 1923; *Chem. Abs.*, 1924, 18, 477. For preparation of resins by electrolysis see British P. 130,608, 1919, to Resan Kunstharz-Erzeug-Ges; *J.S.C.I.*, 1921, 40, 666 A. French P. 518,600, 1919. For voltolization of oils, see Chapter 61.

<sup>97</sup> F. Pollak, U. S. P. 1,211,227, Jan. 2, 1917; *Chem. Abs.*, 1917, 11, 693. U. S. P. 1,369,352, Feb. 22, 1921, to Chemical Foundation, Inc.; *Chem. Abs.*, 1921, 15, 1381.

<sup>98</sup> See also C. W. Rivise, *Plastics*, 1929, 5, 211, 254, 266, 317.

<sup>99</sup> F. Pollak, U. S. P. 1,216,728, Feb. 20, 1917; *Chem. Abs.*, 1917, 11, 1734

<sup>100</sup> B. B. Mashkilleison and S. S. Zimmerman, *Plant. Massw.*, 1932, (1), 32; *Chimie et industrie*, 1932, 29, 1418; *Chem. Abs.*, 1933, 27, 4426.

<sup>101</sup> L. V. Redman, A. J. Weith and F. P. Brock, U. S. P. 1,345,695, July 6, 1920; *Chem. Abs.*, 1920, 14, 2687. See also I. M. Ezrielev and D. B. Khodakova, *Plast Massw.*, 1934, 3, 53; *Chem. Abs.*, 1934, 28, 6579.

<sup>102</sup> F. Pollak, U. S. P. 1,210,982, Jan. 2, 1917; *Chem. Abs.*, 1917, 11, 710. German P. 394,253, 1919. Dutch P. 1,859, 1917.

<sup>103</sup> R. Hessen, U. S. P. 1,816,255, July 28, 1931; *Chem. Abs.*, 1931, 25, 5525. British P. 324,913, 1928; *Chem. Abs.*, 1930, 24, 3914.

hyde to combine completely all the phenol; Ostersetzer and Riesenfeld<sup>103</sup> made powdered hardened resins in emulsified dispersions and thus reduced impurities by decreasing their adsorption of substances from the mother liquor; Moss<sup>104</sup> used sodium phosphate ( $\text{Na}_2\text{HPO}_4$ ) as a condensing agent; Melamid<sup>105</sup> esterified the resins with p-toluenesulphonyl chloride; and Pfautsch<sup>106</sup> treated the phenol itself with sodium bisulphate and thiosulphate and distilled it before use to make light-stable resins. Blumer<sup>107</sup> stabilized the color by oxidizing the resin with persulphates or perborates. Manganese dioxide, lead oxide, lead chromate, sodium chromate, ammonium dichromate and potassium permanganate are said to be useful in maintaining the brilliancy of phenol-formaldehyde resins.<sup>108</sup>

Ehrlich<sup>109</sup> treated the intermediate substances obtained from phenols and formaldehyde with acids (lactic, acetic, tartaric, or boric) to obtain pale-colored resins stable to light and air. The resinous condensation product obtained by heating phenol with 40 per cent formaldehyde solution in the presence of sodium carbonate is washed with hot water until it becomes thick and viscous and then with 4 per cent acetic acid. The resulting thin resin is washed again with water and, after the addition of a small quantity of ammonia, is dehydrated *in vacuo* and hardened in the usual way. The resulting transparent, colorless or faintly yellow material is insoluble in acids and alkalies, and, because of the absence of excess phenol, is stable to light and air.

Distillation of the uncombined phenol from a resin, even under reduced pressure, is ineffective since the last traces are extremely difficult to remove and even small traces are enough to have considerable effect. However, the color-forming constituents are removable from the readily condensable intermediate products before the hardening by extraction with such solvents as ether.<sup>110</sup>

Drummond<sup>111</sup> treated resins made from phenol and formaldehyde with the vapor of an organic solvent (ethyl alcohol), of lower boiling point than water and preferably miscible with the resin, until no further free phenol is removed. The purified substance may be used directly in solution or it may be freed from solvent by heating *in vacuo*.

Purified resins are also obtained by washing successively with hot water, dilute mineral acid, and cold water. The products may be made insoluble by heating to 100°C. or they may be dissolved in appropriate solvents (alcohol, acetone, or amyl acetate) to form varnishes or lacquers. The purified products combine with bases such as lime or ferric oxide, and with glycerol.<sup>112</sup> Bucherer<sup>113</sup> heated phenol-aldehyde resins with a dilute alkaline solution to effect purification.

Various washing procedures were used by Seebach to remove free phenol in purifying resins. Crude fusible phenol-aldehyde compositions may be treated with

<sup>103</sup> A. Ostersetzer and F. Riesenfeld, U. S. P. 1,807,545, May 26, 1931, *Chem. Abs.*, 1931, 25, 4096. German P. 516,877, 1928; *Chem. Abs.*, 1931, 25, 3185. Austrian P. 114,871, 1929; *Chem. Abs.*, 1930, 24, 1189. French P. 651,723, 1928; *Chem. Abs.*, 1929, 23, 3589. British P. 288,228, 1928, *Chem. Abs.*, 1929, 23, 678.

<sup>104</sup> W. H. Moss, U. S. P. 1,743,680, Jan. 14, 1930, to Celanese Corp. of Amer.; *Chem. Abs.*, 1930, 24, 1529. British P. 296,674, 1927, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 1529. See Chapter 16.

<sup>105</sup> M. Melamid, British P. 137,291, 137,292 and 137,293, 1919; *Chem. Abs.*, 1920, 14, 1450, 1451. See also Jacobsohn, *Kunststoffe*, 1921, 11, 105, discussed in Chapter 20.

<sup>106</sup> M. Pfautsch, German P. 341,231, 1919; *J.S.C.I.*, 1922, 41, 93A.

<sup>107</sup> L. Blumer, German P. 217,560, 1908, *Chem. Abs.*, 1910, 4, 1690.

<sup>108</sup> E. E. Novotny, U. S. P. 1,984,423, Dec. 18, 1934, to J. S. Stokes; *Chem. Abs.*, 1935, 29, 855.

<sup>109</sup> O. Ehrlich, German P. 423,032, 1922; *Brit. Chem. Abs.*, 1926, 760.

<sup>110</sup> G. S. Petrov (Russian) P. 31,612 and 31,614, 1933; *Chem. Abs.*, 1934, 28, 3254, 3196. German P. 233,395, 1910, to Bakelite G.m.b.H.; *Chem. Abs.*, 1911, 5, 2745) extracted resins of the fusible type with ethers, benzene, toluene, gasoline or chlorinated hydrocarbons. The resins are then mixed with fillers and pressed.

<sup>111</sup> A. A. Drummond, British P. 274,881, 1926; *Brit. Chem. Abs.*, 1927, 756.

<sup>112</sup> British P. 148,264, 1919, to Soc. Coralex; *Chem. Abs.*, 1921, 15, 319.

<sup>113</sup> H. T. Bucherer, French P. 758,689, 1934; *Chem. Abs.*, 1934, 28, 3256.



alkali<sup>114</sup> or alkaline-earth<sup>115</sup> hydroxides to combine with free phenols and the reaction by-products to form water-soluble salts but no excess is allowed to remain to combine with the resin. Suggested oxides and hydroxides are those of calcium, barium, strontium, magnesium, aluminum, copper, zinc, nickel, or such combinations with alkalies as sodium aluminate, potassium zincate, or sodium zincate. Organic solvents<sup>116</sup> for the resin can be used during or after the action of the metallic oxides, the solvents being completely or incompletely miscible with water as desired. The resins are precipitated by the addition of water, acid or such salts as sodium chloride, magnesium sulphate, alum; or the process may be modified by the addition of salts, such as sodium saheylate or alkali metal soaps which have the property (hydrotropism) of rendering soluble, substances which are insoluble in pure water. The metallic oxides which have not combined with the phenols, Seebach stated, may be allowed to remain in the subsequently precipitated resinous condensation products as filling materials. The process is described approximately as follows:

One hundred kg. of coarsely ground resinous phenol-aldehyde condensation product are mixed for 2 to 3 hours in a ball mill with 200 l. of lime water (containing 6 kg. of quicklime) to form a colloidal solution. The precipitated material is a fine powder which is separated by filtration, centrifuging, or decantation from the liquid and washed with water. The resin may be dried at 30-40°C. This process usually raises the melting point of the resin.

Another proposal by Seebach<sup>117</sup> is the use of fluxing agents in the distillation of permanently fusible resins to free them of uncombined phenols. For this purpose he recommended high-boiling organic substances such as glycerol, ethylene glycol, phthalic, or lactic esters,  $\alpha$ - or  $\beta$ -chloronaphthalene, dichloronaphthalene, tetrahydronaphthalene, decahydronaphthalene, or cyclohexanol and its esters. Fluxes may also include urea or thiourea. For example, 2120 parts of fusible phenol-formaldehyde resin (novolak) and 280 parts of glycerol are distilled *in vacuo*. The distillate amounts to about 306 parts and the residue when cold is almost colorless and free from phenol.

The observation was made by Baekeland<sup>118</sup> that the initial resinous condensation product of phenol when undiluted may be hardened to the infusible condition at temperatures as low as 70°C. When, however, alcohol is added the resulting solution may be boiled under a reflux condenser for a long time without noticeable hardening. Baekeland found that water does not retard the reaction. On heating a solution of phenol-formaldehyde resin in aqueous sodium hydroxide to 80°C. the solution gelatinizes and on further heating hardens rapidly, yielding a transparent infusible product. The solution may be used as a heat-hardening varnish, or may be mixed with appropriate fillers for molding. Seebach<sup>119</sup> observed that a solution of phenol-formaldehyde resin in aniline hydrochloride could be heated for long periods without polymerizing and proposed the following distillation procedure for removing free phenol: 500 kg. of fusible phenol-aldehyde resin are dissolved in a well-stirred solution of 250 kg. of aniline hydrochloride (or salts

<sup>114</sup> F. Seebach, U. S. P. 1,681,368 and 1,681,369, Aug. 21, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1928, 22, 3792. British P. 246,833 and 246,834, 1925; *Brit. Chem. Abs. B.*, 1927, 684, 924. German P. 474,729, 1925; *Chem. Abs.*, 1929, 23, 3114.

<sup>115</sup> F. Seebach, U. S. P. 1,697,885, Jan. 8, 1929, to Bakelite G.m.b.H.; *Chem. Abs.*, 1929, 23, 1294. British P. 248,726, 1926; *Chem. Abs.*, 1927, 21, 828. German P. 432,727, 1925; *Brit. Chem. Abs. B.*, 1927, 259. Swiss P. 126,203, 1926.

<sup>116</sup> F. Seebach, U. S. P. 1,683,702, Sept. 11, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1928, 22, 4262. British P. 247,956 and 247,957, 1925; *Chem. Abs.*, 1927, 21, 660. German P. 431,514, 1925; *Brit. Chem. Abs. B.*, 1926, 859.

<sup>117</sup> F. Seebach, U. S. P. 1,891,455, Dec. 20, 1932, to Bakelite G.m.b.H.; *Chem. Abs.*, 1933, 27, 2001. German P. 545,756, 1928; *Chem. Abs.*, 1932, 26, 3687.

<sup>118</sup> L. H. Baekeland, U. S. P. 1,085,100, Jan. 27, 1914, *Chem. Abs.*, 1914, 8, 1215.

<sup>119</sup> F. Seebach, U. S. P. 1,868,079, July 19, 1932, to Bakelite G.m.b.H.; *Chem. Abs.*, 1932, 26, 5221. German P. 616,766, 1928; *Chem. Abs.*, 1931, 25, 3185.

of other aromatic or aliphatic amines) in 250 kg. of water at 50-60°C. Distillation is then carried out at atmospheric or reduced pressure until 1000-2000 kg. of water have been distilled off, this water being replaced from time to time by additions of hot water to keep the volume unchanged. On adding water to the residue after the phenol has been removed by this distillation, the purified resin is precipitated and the aniline hydrochloride or other salt remains in solution. Organic solvents may be used instead of water and the resins may be washed with hydrotropic salts, if preferred.

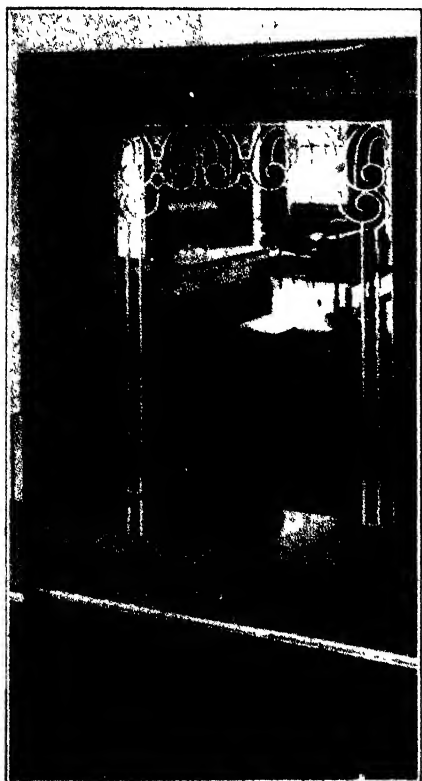


FIG. 63.  
Counter Top and Deal Plate of Formica.

*Courtesy Formica Insulation Co*

For purifying soluble fusible phenol-aldehyde resins, Strafford and Walker<sup>120</sup> incorporated them with an inert filler such as wood flour, cotton waste, asbestos, or china clay and extracted this mixture with water or an organic non-solvent such as benzene. When water is used as the solvent they adjusted it to a  $pH$  of 6 before extraction. After filtering, the extracted material thus treated may be used as a molding powder or the resin may be dissolved out with acetone or alcohol and used in varnishes. The process is also applicable to the purification of sheets impregnated with resin used in making laminated board.

Waterman and Veldman<sup>121</sup> modified this procedure by using a suspension of sawdust in water, into which the liquid condensate was stirred. After agitating

<sup>120</sup> N. Strafford and E. E. Walker, U. S. P. 1,776,202 and 1,776,203, Sept. 16, 1930, to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1930, 24, 5518; British P. 296,514, 1927; *Chem. Abs.*, 1929, 23, 2540. German P. 543,430, 1928; *Chem. Abs.*, 1932, 26, 2561. French P. 656,647, 1928; *Chem. Abs.*, 1929, 23, 4357.

<sup>121</sup> H. I. Waterman and A. R. Veldman, *Chem. Weekblad*, 1934, 31, 492; *Chem. Abs.*, 1935, 29, 519.

for several hours, the resin-sawdust composition was separated by centrifuging, washed and dried. Only a faint odor of phenol or cresol could be detected. Cresol was also satisfactorily removed by employment of a suspension of kieselguhr or fuller's earth in benzene.<sup>129</sup>

The molding powder thus secured is reported to be completely freed of phenolic bodies by treatment with an acid diazonium solution.<sup>129</sup> Two g. of aniline (as hydrochloride) was diazotized with sodium nitrite solution and diluted to 2 liters. This was stirred while cold with 100 g. of the powder, followed by filtration and washing. The odorless product dried to a light brown color.

A bleaching process proposed by Stuhlmann<sup>124</sup> consists in subjecting the resins in cold alkaline solution with continuous stirring to the simultaneous action of formaldehyde and a bleaching agent such as hydrogen peroxide or sodium perborate.

To avoid discoloration of resins in course of manufacture, Kline<sup>125</sup> used acid-resistant materials (glass, porcelain, enamel or chromium) at all points of contact in the reaction apparatus.

#### DEHYDRATION

When a wet process is employed, the final dehydration is usually carried out in the same digester in which the resin is prepared, with or without the help of a vacuum. After the water has been removed, the resin is allowed to flow through a bottom discharge into pans for cooling.<sup>126</sup> If the resin is to be used for varnishes, the dehydrated resin may be left in the digester, solvents added, heat applied, if necessary, and the entire manufacture of the varnish completed in the same kettle. These methods work well with soluble fusible resins of the two-stage type.

The dehydration of the one-stage resin is somewhat more difficult by this procedure, since there is danger of gelatinizing the resin. Various methods have been proposed to overcome this. One consists in agitating the material (containing, e.g., 7 per cent of water) with an amount of propyl alcohol equal to its water content and pouring off the liquid which settles out from the mixture. The water, water-soluble materials, and colored impurities that may be present are removed simultaneously.<sup>127</sup> Another method was proposed by Kulas<sup>128</sup> in which the resin, cooled after separation from the reaction mixture, is centrifuged.

Hessen<sup>129</sup> heated the solid soluble fusible products in thin layers at 100-200°C. for one or more periods of 15-30 seconds with rapid cooling after each heat treatment. In this manner most of the volatile constituents are removed and the resins are partly converted to the insoluble infusible state. This semi-hardened product is subsequently worked up with further hardening agent. Clear transparent moldings are obtained by hot-pressing.<sup>130</sup> Volatile substances can also be

<sup>129</sup> H. I. Waterman, W. Coltof and A. R. Veldman, *Ingenieur*, 1934, 49, MK15; *Chem. Abs.*, 1935, 29, 1532.

<sup>128</sup> H. I. Waterman, W. J. C. de Kok and A. R. Veldman, *Chem. Weekblad*, 1934, 31, 608; *Chem. Abs.*, 1935, 29, 1901.

<sup>124</sup> P. Stuhlmann, U. S. P. 1,809,738, June 9, 1931; *Chem. Abs.*, 1931, 25, 4423. See also German P. 432,252, 1924, to Siemens & Halske.

<sup>125</sup> H. Kline, British P. 353,430, 1929, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 5440.

<sup>126</sup> *Chem. Age (London)*, 1928, 14, 72, 345.

<sup>127</sup> German P. 359,061, 1920, to Wenjact G.m.b.H.; *J.S.C.I.*, 1923, 42, 279A.

<sup>128</sup> C. Kulas, U. S. P. 1,669,831, May 15, 1928; *Chem. Abs.*, 1928, 22, 2475.

<sup>129</sup> R. Hessen, U. S. P. 1,917,713, July 11, 1933, to A. Nowack A.-G.; *Chem. Abs.*, 1933, 27, 4640. German P. 580,560, 1933; *Chem. Abs.*, 1934, 28, 1154. French P. 693,004, 1930; *Chem. Abs.*, 1931, 25, 1645. British P. 350,427, 1930; *Chem. Abs.*, 1932, 26, 5440. See also R. Hessen, British P. 375,396, 1933; *Brit. Chem. Abs. B*, 1933, 808. French P. 713,376, 1932; *Chem. Abs.*, 1932, 26, 1811.

<sup>130</sup> R. Hessen, British P. 353,085, 1932, to A. Nowack A.-G.; *Brit. Chem. Abs. B*, 1933, 79. French P. 728,068, 1931; *Chem. Abs.*, 1932, 26, 5778.

removed by powdering the resin and heating it under vacuum at a temperature below its fusing point.<sup>131</sup>

Spray-drying is said to be advantageous in dehydrating heat-sensitive resins. The aqueous mixture can be sprayed into a stream of air or other gas at 250-300°C. and the dried particles are then rapidly cooled by directing them into a low-temperature zone or upon a cold metal surface.<sup>132</sup>

Novotny<sup>133</sup> also proposed an atomizing or spray-drying process. The material is atomized and quickly wetted by directing the spray into water. The sudden chilling prevents fusion and the water removes impurities. As the solid resin absorbs no moisture the particles are readily separated from the wash water. The surface moisture on the resinous particles is quickly removed and the product easily dried. For drying a relatively wet, sludge-like synthetic-resin mass containing occluded water or mother liquor, Novotny cooled it, by mechanical refrigeration preferably, to a temperature at which it becomes solid and can be mechanically ground, but below that at which the ground particles agglomerate. The finely ground particles are then dehydrated by air currents. This type of drying is said to be particularly useful for resins made by the one-stage wet process. Petrov<sup>134</sup> suggested dehydrating by heating resins to 100-180°C. in a medium of drying or semi-drying oils under ordinary or reduced pressure.

#### SOLUBLE RESINS FROM INSOLUBLE

A method for converting an infusible product into a fusible one after the reverse change has once occurred was developed by Aylsworth.<sup>135</sup> An infusible porous mass, made by heating phenol, formaldehyde (40 per cent aqueous solution) and a small amount of either an acid or a basic catalyst, is ground and baked at 175°C. to remove entrapped water and acid vapors. This product is heated for several hours at 230-290°C. in a closed vessel with approximately one-half its weight of phenol or cresol. By this treatment the resin is dissolved and converted into a fusible form. A mixture of phenol and naphthalene may be substituted for phenol or cresol as the solvent. If naphthalene is used, it is later removed by distillation. This method can be used advantageously to reclaim discarded or imperfect articles or scrap containing an infusible resin binder.<sup>136</sup>

Kulas and Pauling<sup>137</sup> accomplished a similar conversion by heating finely powdered infusible resins, free from lumps, with phenols at atmospheric pressure until they are either dissolved or converted into a uniform swollen paste and resinifying the free phenol by the addition of formaldehyde and an acid or basic catalyst. Heating a phenol-formaldehyde resin with dihydroxybiphenyl in the presence of manganese dioxide, yields a composition which is characterized by its solubility in fatty oils.<sup>138</sup>

Becherer<sup>139</sup> proposed heating an insoluble phenol-urea-formaldehyde compound with a phenol until dissolved (and partially reacted). Sulphonation of the resultant liquid yielded material applicable as a mordant or tanning agent.

A procedure which is applicable to masses containing cellulose filler is to heat them in an autoclave with a phenol and a substance which hydrolyzes the

<sup>131</sup> M. Koebner, U. S. P. 1,981,514, Nov. 20, 1934, to F. Raschig G.m.b.H.; *Chem. Abs.*, 1935, 29, 526. British P. 416,847, 1934; *Chem. Abs.*, 1935, 29, 1176. French P. 751,161, 1933; *Chem. Abs.*, 1934, 28, 1208.

<sup>132</sup> British P. 408,689, 1932, to Bakelite Corp.; *Brit. Chem. Abs.* B, 1934, 546.

<sup>133</sup> E. E. Novotny, U. S. P. 1,771,139 and 1,771,140, July 22, 1930; *Chem. Abs.*, 1930, 24, 4648.

<sup>134</sup> G. S. Petrov, Russian P. 4328, 1923; *Chem. Abs.*, 1923, 22, 4740; 1932, 26, 2561.

<sup>135</sup> J. W. Aylsworth, U. S. P. 1,027,794, May 28, 1912; *Chem. Abs.*, 1912, 6, 2010. German P. 258,250, 1911; *Chem. Abs.*, 1912, 6, 2010.

<sup>136</sup> See also C. W. Rivise, *Plastics*, 1928, 4, 309.

<sup>137</sup> C. Kulas and C. Pauling, German P. 412,170, 1923; *J.S.C.I.*, 1925, 44, 729B.

<sup>138</sup> F. Seebach, U. S. P. 1,971,507, Aug. 28, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 6580.

<sup>139</sup> F. Becherer, U. S. P. 1,982,619, Dec. 4, 1934, to J. R. Geigy, S. A.; *Chem. Abs.*, 1935, 29, 525.

cellulose (10 per cent hydrochloric acid). The product is rinsed with water and can be converted into a moldable resin by addition of hexamethylenetetramine.<sup>140</sup>

Infusible resins are also completely converted into fusible resins by heating them with aqueous alkalies to a temperature above the boiling point of the solution.<sup>141</sup> For example, 100 kg. of coarsely powdered infusible resin may be heated with 1000 l. of 5 per cent sodium hydroxide solution at 200°C. for 1 hour to accomplish this conversion.<sup>142</sup>

Sections of infusible and substantially insoluble condensation products may be united by moistening the faces to be joined with a liquid such as acetone or alcohol, coating the surfaces with fusible phenol-formaldehyde resin and heating the faces pressed together until the intervening film becomes infusible.<sup>143</sup>

<sup>140</sup> British P. 397,690, 1932, to Philips' Gloeilampenfabr.; *Brit. Chem. Abs.* B, 1933, 929. French P. 743,859, 1933, *Chem. Abs.*, 1933, 27, 4110. German P. 605,124, 1934, *Chem. Abs.*, 1935, 29, 1176.

<sup>141</sup> German P. 523,191, 1928, to F. Raschig G m b H; *Chem. Abs.*, 1931, 25, 3448.

<sup>142</sup> Insoluble resins can also be made soluble by fluxing them with rosin. See Chapter 19.

<sup>143</sup> L. V. Redman, A. J. Weith and F. P. Brock, U. S. P. 1,424,738, Aug. 1, 1922; *Chem. Abs.*, 1922, 16, 3370.

# Chapter 16

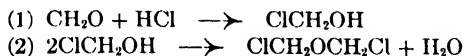
## Phenol-Aldehyde Resins

### IV. Catalysts

The production of resins from phenol and formaldehyde is customarily accomplished with the aid of catalytic bodies. One of the important factors in determining the course of the condensation reaction is the nature of the catalyst employed. It has been noted by Baekeland<sup>1</sup> (see also Chapter 14) that acid catalysts favor the following series of reactions: phenol + formaldehyde  $\longrightarrow$  hydroxyphenylphenoxymethane (rearranges to dihydroxydiphenylmethane)  $\longrightarrow$  soluble, fusible product (Novolak)  $\xrightarrow{\text{HCHO}(\pm\text{NH}_4)} \text{Resinoid A} \xrightarrow{\text{heat}} \text{Resinoid B} \xrightarrow{\text{heat}} \text{Resinoid C}$  (infusible, insoluble). In the presence of alkali, the condensation tends to take place in the following stages: phenol + formaldehyde  $\longrightarrow$  hydroxybenzyl alcohol  $\xrightarrow{\text{heat}} \text{Resinoid A}$  (can be melted a limited number of times)  $\xrightarrow{\text{heat}} \text{Resinoid B}$  (becomes jelly-like with solvents)  $\xrightarrow{\text{heat}} \text{Resinoid C}$ .

It is immediately apparent that certain steps in the condensation process are more or less selectively favored by particular types of catalysts. While no complete theory correlating all the facts of acid and basic catalysis in the field of the phenolic resins has yet been advanced, nevertheless there exists a considerable amount of scattered information on the subject. The catalytic effects of acid and basic molecules<sup>2</sup> come into play in a very large number of chemical reactions. It is believed by Brönsted that these catalytic effects, often ascribed to hydrogen ions, are in reality caused by -onium ions of the  $\text{OH}_2^+$  type. (See also Chapter 4.)

Hydrochloric acid reacts with formaldehyde (in the absence of phenol) in such a manner as to leave the methylene group intact. The compounds which have been isolated from this reaction are dichlorodimethyl ether<sup>3</sup> and an ether of the structure  $\text{ClCH}_2\text{OCH}_2\text{OCH}_2\text{OCH}_2\text{Cl}$  Blanc<sup>4</sup> assumes that the initial product is chloromethyl alcohol, which is too easily hydrolyzed to accumulate in water solution. The mechanism<sup>5</sup> would then be:



The formation of these compounds is quoted at this point in order to illustrate the fact that formaldehyde has been found to have a different type of reactivity in acids than it has in alkaline solution. It is not to be implied that chloromethyl alcohols or ethers are intermediates in the phenol-aldehyde condensation. In dilute

<sup>1</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1909, 1, 1545.

<sup>2</sup> J. N. Brönsted, *Svensk Kém. Tid.*, 1928, 40, 230, *Brit. Chem. Abs. A*, 1928, 1195 J. N. Brönsted and E. A. Guggenheim, *J. A. C. S.*, 1927, 49, 2554

<sup>3</sup> F. M. Litterschied and K. Thimme, *Ann.*, 1904, 334, 40; *Chem. Zentr.*, 1904, 2, 949

<sup>4</sup> G. Blanc, *Bull. soc. chim.*, 1923, 33, 313; *Chem. Abs.*, 1923, 17, 2103. *American Perfumer*, 1923, 17, 541; *Perfumery Essential Oil Record*, 1923, 14, 40; *Chem. Abs.*, 1923, 17, 1630.

<sup>5</sup> W. Tsihtchenko, *J. Russ Phys.-Chem. Soc.*, 1887, 19, 470; *J.C.S.*, 1888, 54, 804. A. Moersch, *Atti. accad. Lincei*, 1919, 28 (1), 277; *J.C.S.*, 1919, 116 (1), 385.

alkaline solution, as is well known, formaldehyde undergoes polymerization which involves the reallocation of methylene hydrogens upon carbonyl oxygens.<sup>6</sup> Thus, formaldehyde exhibits two contrasting modes of reaction, depending on whether it is in acid or basic solution. This observation is in harmony with the fact that the course of the phenol-formaldehyde reaction depends in part upon the acidity or alkalinity of the catalyst.

Ordinarily, the choice of catalyst is governed by more pragmatic considerations than would be indicated in a study of the reaction mechanism. The early controversies and patent litigations probably drew attention to a wider variety of catalysts than might otherwise have been investigated. Furthermore, important properties of the resins could be varied by varying the nature or quantity of the catalyst. Both strongly acid and strongly basic condensing agents when used in large proportions affect metals, cause deterioration of fillers and attract moisture. Their presence is particularly objectionable in resins which are to be used as dielectrics. In the pages to follow mention will be made of many of the mineral acids, organic acids, acid and basic salts which have been recommended. Also, various alkaline materials, ammonia and ammonium compounds, ammonium derivatives, various amines, particularly methylamines, aniline and benzylamine, have been employed, and their applications as catalysts will be described in this chapter.

#### EARLY WORK ON CATALYSTS FOR THE PHENOL-FORMALDEHYDE REACTION

The early investigators, who studied the phenol-aldehyde condensation as a possible (but often disappointing) means of synthesizing crystalline compounds, used acid catalysts.<sup>7</sup> Baeyer<sup>8</sup> called attention to the resin which was formed when phenol reacted with formaldehyde in the presence of hydrochloric acid. He further observed that resorcinol and formaldehyde, in the presence of hydrochloric acid, gave an insoluble body which burned without melting. In these experiments, the formaldehyde was used in the form of the monoacetate of dihydroxymethane. Ter Meer<sup>9</sup> found that, through the use of a mixture of glacial acetic and sulphuric acids, methylal could be condensed with anisol, and di-(methoxyphenyl)-methane could be isolated. Kleeberg<sup>10</sup> reported that alkali-insoluble resins were obtained by reacting formaldehyde with phenol, resorcinol or catechol in the presence of hydrochloric or sulphuric acids. Hosaeus,<sup>11</sup> working with the reaction between  $\beta$ -naphthol and formaldehyde, to form methylenedi- $\beta$ -naphthol, found that strong acids were not necessary as catalysts, and that glacial acetic acid served the purpose.  $\alpha$ -Naphthol condensed with formaldehyde in the presence of acetic acid to form a yellow alkali-soluble resin.<sup>12</sup>

Lederer<sup>13</sup> proposed the use of alkaline catalysts in the phenol-formaldehyde condensation, and by employing milk of lime or baryta water he was able to prepare crystalline hydroxybenzyl alcohols. Manasse prepared a series of phenol alcohols by condensing homologues of phenol with formaldehyde in the presence of caustic soda, caustic potash, potassium or sodium carbonates, quicklime, zinc and lead oxides, zinc dust, sodium acetate or potassium cyanide.<sup>14</sup> The phenol alcohols were converted into resins by the action of heat.

<sup>6</sup> O. Loew, *Ber.*, 1886, 20, 141.

<sup>7</sup> See Chapter 13.

<sup>8</sup> A. Baeyer, *Ber.*, 1872, 5, 1095.

<sup>9</sup> E. ter Meer, *Ber.*, 1874, 7, 1200.

<sup>10</sup> W. Kleeberg, *Ann.*, 1891, 263, 283; 264, 351.

<sup>11</sup> H. Hosaeus, *Ber.*, 1892, 25, 3212.

<sup>12</sup> J. Abel, *Ber.*, 1892, 25, 3477.

<sup>13</sup> L. Lederer, *J. prakt. Chem.*, 1894, (2) 50, 224. U. S. P. 563,975, July 14, 1896.

<sup>14</sup> O. Manasse, *Ber.*, 1894, 27, 2409. U. S. P. 526,786, Oct. 2, 1894. German P. 85,588, 1894, to Farbenfabriken vorm. F. Bayer & Co.

## BASIC CATALYSTS

After phenol-formaldehyde products began to be commercialized, it was pointed out<sup>15</sup> that the addition of an organic or inorganic base in proper proportion to a mixture of phenol and formaldehyde yields products which have technical advantages over those obtained by simple heating or by the use of acids or salts as condensing agents. A wide variety of alkaline materials (e.g., ammonia, caustic alkali, alkali sulphites) was used, the quantities recommended by Baekeland being 0.5-10 per cent, and in no case above 20 per cent of the total reaction mixture. The products were usually semi-solid and could be converted into insoluble, infusible resins by heating at 120-200°C. under pressure. The undesirable properties of phenol-formaldehyde resins made through the use of strong caustic as a catalyst can be avoided in various ways. For instance, it is possible<sup>16</sup> to use proportions of alkali exceeding 20 per cent of the total weight of the reaction mixture, provided the excess alkali is neutralized with acid after the resin has formed. When such large amounts of alkali are used, subsequent neutralization can be effected not only by strong acid but by the addition of salts of aluminum, zinc, copper, iron, lead, nickel or cobalt, since these metals yield insoluble hydroxides.<sup>17</sup> Similarly, Stockhausen and Grühl used ferric and aluminum chlorides to control the degree of plasticity of phenol-formaldehyde resins made in the presence of caustic soda.<sup>18</sup> Alternatively,<sup>19</sup> excess alkali can be neutralized with stearic acid, a practice which, according to Aylsworth, results in resins of good insulating properties. Van Voorhout condensed phenol and formaldehyde with 0.5 per cent caustic soda, and avoided excess brittleness by adding glycerol and turpentine,<sup>20</sup> or by cooling the products before the condensation had progressed too far. This cooling was conveniently accomplished by adding alcohol, and then distilling it off in a current of air.

It should be noted that when the products of alkaline condensation of phenol and formaldehyde are treated with acids, certain difficulties in operating conditions must be taken into account.<sup>21</sup> As the liquid reaction mixture begins to thicken, stirring becomes extremely difficult or impossible. Consequently hardening tends to occur unequally throughout the mass. If very small quantities of acid are used, the difficulty is not so great, but the hardening requires a long time. Large quantities of acid not only cause non-uniform products, but also blistering and sticking in the mold. Because of these considerations, the acidification was carried out by Schmidt in the following manner. After the initial resin had been formed in the presence of 2 per cent caustic soda, the reaction mixture was neutralized by adding hydrochloric acid. Water was removed by vacuum distillation, and the liquid resin was drawn off and poured into a kneading machine. A small excess of acid (2 per cent of phosphoric or oxalic acids) was introduced. After the kneading operation, the mass was hardened in a rod press (see Chapter 67) or cooled and ground to form a molding powder.

<sup>15</sup> L. H. Baekeland, U. S. P. 942,809, Dec. 7, 1909, *Chem. Abs.*, 1910, 4, 680. German P. 281,454, 1908; *J.S.C.I.*, 1909, 28, 374. British P. 21,566, 1908; *J.S.C.I.*, 1909, 28, 374. H. Lebach, British P. 28,009, 1907, to Knoll & Co.; *J.S.C.I.*, 1908, 27, 908. French P. 395,657, 1903, to Knoll & Co.; *J.S.C.I.*, 1909, 28, 483.

<sup>16</sup> French P. 361,539, 1905, to Fabr. de produits de chim. org. de Laire; *Chem. Abs.*, 1907, 1, 1181.

<sup>17</sup> L. H. Baekeland, U. S. P. 1,187,229, June 13, 1916; *Chem. Abs.*, 1916, 10, 2030.

<sup>18</sup> H. Stockhausen and R. Grühl, U. S. P. 1,150,642, Aug. 17, 1915; *Chem. Abs.*, 1915, 9, 2699. British P. 14,481, 1913; *Chem. Abs.*, 1915, 9, 164.

<sup>19</sup> J. W. Aylsworth, U. S. P. 1,146,300, July 13, 1915; *Chem. Abs.*, 1915, 9, 2432. Canadian P. 160,736 to 160,740, 1915; *Chem. Abs.*, 1915, 9, 2132.

<sup>20</sup> A. W. C. van Voorhout, U. S. P. 1,271,392 and 1,271,393, July 2, 1918; *Chem. Abs.*, 1918, 12, 1916.

<sup>21</sup> F. Schmidt, U. S. P. 1,927,375, Sept. 19, 1932; *Chem. Abs.*, 1933, 27, 5907. F. Schmidt, U. S. P. 1,978,821, Oct. 30, 1934. E. S. Hole, British P. 278,460, July 16, 1926. French P. 678,250, to Chemie & Technik JMS G. m. b. H. Waldemar Steffen, *Chem. Abs.*, 1930, 24, 3663.



Kulas and Pauling<sup>22</sup> prepared fusible soluble resins as initial condensation products of phenol and formaldehyde in alkaline solution. These resins were heated in molds at 80-100°C. under pressure, and became hard, but were still fusible and soluble. Conversion to infusible insoluble products was accomplished by heating at 120-140°C. at ordinary pressure.

In strongly alkaline condensations, the formaldehyde may react to form phenol alcohols or it may undergo a Cannizzaro reaction, forming methyl alcohol and alkali formate. The extent to which the latter type of reaction takes place is reduced by operating at low temperatures.<sup>23</sup>

Ammonia and its derivatives are the catalysts<sup>24</sup> perhaps most commonly used in commercial production of phenol-aldehyde resins, for these agents cause no undesirable degree of acidity or alkalinity. As noted in Chapter 13, the use of ammonia in similar condensation reactions had its beginnings prior to 1900. The present discussion will be limited to those investigations which seem to be best dealt with under the heading of catalysts. A considerable percentage of the total number of patents in the field of the phenol-formaldehyde resins make some mention of the possible use of ammonia or hexamethylenetetramine in conjunction with the particular process described. These processes are discussed in their appropriate chapters. As a permanent constituent of phenolic resins, ammonia is less objectionable than fixed alkalis. This fact is particularly true if the resins are to be used for their electrical properties.<sup>25</sup> Aylsworth<sup>26</sup> proposed the addition of phthalic anhydride as a means of neutralizing free ammonia. Paqué<sup>27</sup> noted a particular advantage in using ammonia as the catalyst, for the resins he obtained were permanently clear. These products were prepared by subjecting the intermediate resin to a pressure of 100 atmospheres at 130°C. It has been recommended<sup>28</sup> that the quantity of ammonia employed in condensing phenol and formaldehyde be from 1-10 per cent of the weight of the total reaction mixture. If aniline is used in place of ammonia, the quantity required is from 1-5 per cent. Wiechmann<sup>29</sup> obtained a condensation product which was viscous and syrupy at ordinary temperatures, anhydrous, non-hygroscopic and insoluble in water, when 100 parts of crystallized carboic acid were heated with 10-35 parts of paraform in the presence of dry ammonia. Filhol<sup>30</sup> produced infusible condensation products from phenols and formaldehyde by using ammonia or ammonium carbonate as a catalyst at 75-80°C. When the viscosity of the mixture had increased considerably, an acid catalyst, particularly ethyl sulphuric acid, was added. The final product was obtained by heating at a slightly raised temperature. The ethyl sulphuric acid may be added in alcohol solution, and the product used as a varnish. Also, a number of basic compounds, both organic and inorganic, were proposed, namely, strontium, cupric and aluminum hydroxides, pyridine, various cyanides, urea, guanidine carbonate and piperidine dithiocarbamate.

A light-colored resin was made by Kunisch<sup>31</sup> by condensing phenol and formaldehyde in the presence of ammonia and hydrogen sulphide, with the addition of carbon disulphide.

<sup>22</sup> C. Kulas and C. Pauling, British P. 203,733, Apr. 12, 1922; *J.S.C.I.*, 1923, 42, 1081A.

<sup>23</sup> F. S. Granger, U. S. P. 1,946,459, Feb. 6, 1934, to Combustion Utilities Corp.; *Brit. Chem. Abs.* B, 1934, 1022.

<sup>24</sup> L. H. Baekeland, U. S. P. 942,809, Dec. 7, 1909; *Chem. Abs.*, 1910, 4, 680.

<sup>25</sup> T. Hanyu, *Researches Electrotech. Lab. (Tokyo)*, 1929, 262, 24; *Chem. Abs.*, 1930, 24, 2621.

<sup>26</sup> J. W. Aylsworth, U. S. P. 1,020,594, Mar. 19, 1912 and 1,102,634, July 7, 1914; *Chem. Abs.*, 1912, 6, 1377; 1914, 8, 3127.

<sup>27</sup> F. Paqué, Australian P. 8096 to 8099, 1909; *Chem. Abs.*, 1912, 6, 2010. S. Sugimoto, *Repts. Imp. Ind. Research Inst. Osaka (Japan)*, 1926, 7 (1), 1; *Chem. Abs.*, 1926, 20, 3541.

<sup>28</sup> German P. 281,454, Jan. 8, 1915, to Bakelite G. m. b. H.; *Chem. Abs.*, 1915, 9, 2133.

<sup>29</sup> F. C. Wiechmann, U. S. P. 1,080,183, Dec. 2, 1913; *Chem. Abs.*, 1914, 8, 433.

<sup>30</sup> J. Filhol, British P. 147,173, 1920; *Chem. Abs.*, 1920, 14, 3769.

<sup>31</sup> H. Kunisch, French P. 246,568, 1911; *J.S.C.I.*, 1911, 30, 946.

Fifteen to 45 cc. of carbon disulphide were added to 0.5 kg. of melted crystallized phenol,  $\frac{1}{4}$ -% l. of water saturated with hydrogen sulphide was introduced, then 0.5 kg. of 40 per cent formaldehyde, and finally  $\frac{1}{8}$  kg. of pure 24 per cent ammonia solution. The mixture was heated for 1-2 hours at  $140^{\circ}\text{C}$ ., allowed to cool, and the upper aqueous layer separated. The lower layer was heated for 12 hours at  $100$ - $110^{\circ}\text{C}$ ., and when cool was broken up, heated in molds to a temperature of  $150$ - $200^{\circ}\text{C}$ ., and submitted to a pressure of 150-300 atmospheres. The hydrogen sulphide may be replaced by thiophenol or other substances which evolve hydrogen sulphide under the conditions of the reaction. It is said to be advantageous to add to the mixture a metallic oxide or sulphide, preferably zinc oxide, in the proportion of 5-20 g. per kg. of phenol, omitting ammonia and hydrogen sulphide.

Ammonia may be used in conjunction with caustic alkali. When a mixture of ammonia and potassium hydroxide is the condensing agent,<sup>32</sup> there is obtained a resin whose surface color changes gradually upon exposure to an oxidizing atmosphere.

Cherry<sup>33</sup> stated that by using a mixture of a fixed base, such as caustic soda and slaked lime, and aniline potentially reactive resins are obtained which when molded under heat and pressure yield products hardening rapidly at lower temperatures and possessing greater strength than when ammonia is used alone.

Hexamethylenetetramine is stated to be essentially equivalent to a mixture of ammonia and formaldehyde in the phenol-formaldehyde reaction.<sup>34</sup> Salts of this amine (hydrochloride, sulphate, tartrate, oxalate) have been recommended. It was suggested<sup>35</sup> that these salts be used in quantity not exceeding 2 per cent of the weight of the resin ingredients. Hexamethylenetetramine is often used as a hardening agent for resins which may have been produced through the use of other catalysts. Thus, soluble fusible resins are combined with not more than 5 per cent hexamethylenetetramine in order to harden them.<sup>36</sup>

In the preparation of colorless resins, hydrazine may be used in place of ammonia.<sup>37</sup> Alternatively, hydroxylamine may be employed.<sup>38</sup> Rossiter and Davis<sup>39</sup> condensed phenols, in the presence of 1-10 per cent of their weight of dicyanodiamide, with aldehydes. In one example they heated 40 parts of phenol and 2 parts of dicyanodiamide dissolved in 27 parts 40 per cent formaldehyde at  $70$ - $80^{\circ}\text{C}$ . with agitation for 4-5 hours. The mixture was evaporated, or the aqueous layer was separated and the resin dried. A transparent product was obtained which was soluble in alcohol and could be converted into a hard transparent insoluble resin by heating at  $100$ - $120^{\circ}\text{C}$ .

Aminophenols were used by Baekeland for the purpose of assisting the condensation of phenols with formaldehyde.<sup>40</sup> Thus, hexamethylenetetraminetriphenol not only acts as a catalyst but provides a portion of the reactants also. Phenol derivatives containing basic groups in addition to hydroxyl groups (amino-

<sup>32</sup> H. V. Potter, British P. 131,112, 1918, to Damard Lacquer Co.; *Chem. Abs.*, 1920, 14, 104. T. Shono, *J.S.C.I.* (Japan), 1926, 29, 121; *Chem. Abs.*, 1926, 20, 2419.

<sup>33</sup> O. A. Cherry, U. S. P. 1,994,753, Mar. 19, 1935, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 3073.

<sup>34</sup> L. H. Baekeland and N. Thurlow, U. S. P. 1,187,231, June 13, 1916, to General Bakelite Co.; *Chem. Abs.*, 1916, 10, 2031. Hexamethylenetetramine, 1 mol, ethyl alcohol, 12 mols, and hydrochloric acid, 4 mols, yield ethylal. When ethyl alcohol is replaced by phenol, an acetal of the formula  $\text{CH}_2(\text{OC}_6\text{H}_5)_2$ , and resinous condensation products are formed. See also Chapter 17. E. Defrance, *J. Pharm. Belg.*, 1921, 3, 605; *Chem. Abs.*, 1921, 15, 3891.

<sup>35</sup> W. H. Nuttall, British P. 160,258, 1919, to Vickers, Ltd., and to Ioco Rubber & Proofing Co., Ltd.; *J.S.C.I.*, 1921, 40, 358A.

<sup>36</sup> A. A. Samuel, French P. 700,789, 1929; *Chem. Abs.*, 1931, 25, 3856.

<sup>37</sup> W. H. Nuttall, *loc. cit.*

<sup>38</sup> H. Lobach, *J.S.C.I.*, 1913, 32, 560.

<sup>39</sup> E. C. Rossiter and C. Davis, U. S. P. 1,857,478, May 10, 1932, to British Cyanides, Ltd.; *Chem. Abs.*, 1932, 26, 3945. British P. 327,154, 1928; *Chem. Abs.*, 1930, 24, 5173. French P. 686,261; *Chem. Abs.*, 1932, 26, 611.

<sup>40</sup> L. H. Baekeland, U. S. P. 1,354,154, Sept. 28, 1920; *Chem. Abs.*, 1921, 15, 153.

phenols, methylaminophenols, hydroxyquinoline, hydroxydiphenylamine) have been proposed as catalysts.<sup>41</sup>

The alkyl and aryl amines have been investigated to a considerable extent. The condensation of naphthol with formaldehyde was carried out by Helm<sup>42</sup> with amines or ammonium salts, the proportions being as follows. Two hundred and ninety parts of naphthol were dissolved in 150 parts of a 40 per cent solution of formaldehyde and 95 parts of aniline were added. The resinous product was proposed for use as a shellac substitute. Xylidines, toluidines, benzidine and diphenylamine are said to retard the hardening of resinous mixtures made from phenol and hexamethylenetetramine.<sup>43</sup> These aromatic amines are added at an intermediate stage in the condensation. Bender<sup>44</sup> reacted phenol with anhydroformaldehyde-aniline,  $(C_6H_5NCH_2)_2$ , the weight of the latter being twice the weight of phenol used, and a fusible potentially-reactive resinous product was formed. The aniline was removed at 210°C. without causing the resin to become infusible. Holmes and Megson<sup>45</sup> studied the comparative rates of condensation of various phenols in the presence of catalysts. With trimethylamine, the following increasing order of reactivity was established: p-cresol, phenol, o-cresol, m-cresol, symmetrical xlenol (*cf.* Chapter 17). Contrary to expectation, o-cresol did not show especial sluggishness, although it yielded less highly condensed products. A similar ordination was obtained when triethylamine was used as the condensing agent. With pyridine as a catalyst, the relative reactivity of o-cresol was different from that noted in the above series, for it condensed less rapidly than phenol and at a rate essentially the same as p-cresol. In one series of experiments the various catalysts used were (in the order of their increasing effectiveness) pyridine, ammonia, triethanolamine, isopropylamine, tripropylamine, n-propylamine, methylamine, ethylamine, dipropylamine, piperidine, diethylamine, triethylamine, trimethylamine, methylamine, sodium hydroxide and sodium carbonate.

Regal<sup>46</sup> condensed phenol and formaldehyde in the presence of compounds formed by the action of formaldehyde on tertiary aromatic amines. Dimethylaniline, 2 parts, for example, was boiled with 400 parts by weight of 40 per cent formaldehyde solution. One hundred to 150 parts of hexamethylenetetramine and about the same quantity of paraformaldehyde were then added and boiling continued. The formaldehyde stock was caused to react with 1000 parts of phenol. Edison<sup>47</sup> hardened phenolic resins by adding p-phenylenediamine in the proportion of 0.5-1 per cent of the total resin ingredients. Pyridine was used as a catalyst by Morgan and Megson<sup>48</sup> in condensing fractions of low-temperature tar with formaldehyde. Products which are rendered infusible and insoluble by heat and pressure were obtained when phenols were condensed with aldehydes in the presence of butylamine, monoethanolamine, diethanolamine, cyclohexylamine, dicyclohexylamine, cyclohexylethanolamine or dicyclohexylethanolamine.<sup>49</sup>

The use of an indophenol or indamine was proposed by Regal.<sup>50</sup> The catalyst was formed *in situ* by the reaction between p-aminodimethylaniline and phenol, followed by treatment with an oxidizing agent. One part of p-aminodimethylaniline

<sup>41</sup> German P. 358,195, 1919, to Felten & Guilleume Carlswerke A.-G.; *J.S.C.I.*, 1922, 41, 948A. *Chem. Met. Eng.*, 1922, 29, 33.

<sup>42</sup> L. Helm, French P. 392,395, 1907; *J.S.C.I.*, 1908, 27, 1912. British P. 25,216, 1907; *J.S.C.I.*, 1908, 27, 412.

<sup>43</sup> British P. 363,694, 1930, to Bakelite Corp.; *Brit. Chem. Abs.* B, 1932, 272.

<sup>44</sup> H. L. Bender, U. S. P. 1,955,731, April 24, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 4256.

<sup>45</sup> E. L. Holmes and N. J. L. Megson, *J.S.C.I.*, 1933, 52, 415T.

<sup>46</sup> A. Regal, U. S. P. 1,584,473, May 11, 1926; *Chem. Abs.*, 1926, 20, 2082. British P. 256,394, 1925; *Chem. Abs.*, 1927, 21, 2993.

<sup>47</sup> T. A. Edison, U. S. P. 1,283,706, Nov. 5, 1918; *Chem. Abs.*, 1919, 13, 169.

<sup>48</sup> G. T. Morgan and N. J. L. Megson, *J.S.C.I.*, 1931, 50, 191T. See Chapter 17.

<sup>49</sup> British P. 302,609, 1927, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1929, 23, 4308. K. Seydel, German P. 537,452, 1927, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1932, 26, 1077.

<sup>50</sup> A. Regal, U. S. P. 1,584,472, May 11, 1926; *Chem. Abs.*, 1926, 20, 2082. British P. 254,888, 1925; *Chem. Abs.*, 1927, 21, 2809. Canadian P. 262,930, 1926; *Chem. Abs.*, 1926, 20, 3581.

was heated for 1 hour on the steam bath with 1000 parts by weight of phenol. A small amount (0.05 part) of potassium permanganate was then added, followed by 800 parts of 40 per cent formaldehyde solution. The mixture was heated further until resinification had taken place. The resin obtained was of a bluish or green color, which coloration could be destroyed by the addition of dilute mineral acids. Acetanilide was used as catalyst by Hechtman.<sup>51</sup> Furfuramide<sup>52</sup> and hydrobenzamide have also received attention. Greenwald<sup>53</sup> made use of triethanolamine by mixing 100 parts cresol, 100 parts formaldehyde and 7.5 parts triethanolamine, and carrying out the reaction at approximately 100°C. After 60 minutes the supernatant aqueous solution was withdrawn, and the viscous resin was dried *in vacuo*. Fillers were added, and the mixture was hardened in molds at 100-140°C. It has been recommended<sup>54</sup> that 4 per cent urea, and a salt (e.g., KBr) be added to resins made by condensing cresols with formaldehyde in the presence of triethanolamine (see Chapter 17). Comparative experiments are said<sup>55</sup> to indicate that resins made from low temperature tars using triethanolamine as a condensing agent have lower break-down voltages than the corresponding resins made with trimethylamine or methylamine.

Singer<sup>56</sup> catalyzed phenol-formaldehyde condensations by means of chloroaminoaldehydes. Colorless resins were obtained by Jäger<sup>57</sup> by the use of ammonia as the principal condensing agent with the subsequent addition of dithiocarbamates of strong bases such as piperidine pentamethylenedithiocarbamate, dimethylaminedimethyldithiocarbamate or diethylaminedimethyldithiocarbamate.

#### ACID CATALYSTS

When condensation of phenol and formaldehyde is carried out with a strongly alkaline catalyst, acid may be added at an intermediate stage in order to neutralize the excess alkali (*vide supra*). When this is done, the rate of reaction is diminished, but if additional quantities of acid are introduced, acid catalysis begins to be effective, and an increase in rate ensues. Near the neutral point, the course of the reaction is such as to yield products which are converted into infusible masses by heat. Increasing the amount of acid results in formation of saliretins (Novolaks). Still further increasing the proportion of acid directs the course of the reaction to the formation of infusible resins.<sup>58</sup>

Lebach<sup>59</sup> found it advisable to prepare first a liquid condensation product of phenol and formaldehyde, this being accomplished ordinarily in the presence of alkali. Addition of hydrochloric acid caused solidification to take place. Blocks for newspaper printing were made in this manner. The liquid resin was found to penetrate the remote parts of the most delicate molds, so that very true replicas could be made. Eilersten<sup>60</sup> fused phenols with trioxymethylene, and treated

<sup>51</sup> I. E. Hechtman, Russian P. 23,617, 1931; *Chem. Abs.*, 1932, 26, 2073.

<sup>52</sup> O. Cheriv and F. Kurath, U. S. P. 1,737,916, Dec. 3, 1929, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1930, 24, 929. U. S. P. 1,710,722, Apr. 30, 1929, *Chem. Abs.*, 1929, 23, 3080. Canadian P. 280,359, 1928 and 280,543, 1928; *Chem. Abs.*, 1928, 22, 2819. F. Kurath, U. S. P. 1,726,671, Sept. 3, 1929, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1929, 23, 5283. E. E. Novotny and D. S. Kendall, U. S. P. 1,705,496, Mar. 19, 1929, to J. S. Stokes; *Chem. Abs.*, 1929, 23, 2309. See also Chapter 24. E. C. Rossiter and C. Davis, U. S. P. 1,857,473, May 10, 1932, to British Cyanides, Ltd.; *Chem. Abs.*, 1932, 26, 3945. British P. 327,154, 1928; *Chem. Abs.*, 1930, 24, 5173. French P. 698,261, 1929; *Chem. Abs.*, 1931, 25, 611.

<sup>53</sup> W. F. Greenwald, U. S. P. 1,873,575, Aug. 23, 1932; *Chem. Abs.*, 1932, 26, 6166. See also French P. 707,433, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 861.

<sup>54</sup> German P. 595,571, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 5264.

<sup>55</sup> *Chem. Age (London)*, 1932, 27, 634.

<sup>56</sup> R. Singer, U. S. P. 1,590,961, June 29, 1926, to Kunstharzfabrik Regal & Co.; *Chem. Abs.*, 1926, 20, 3091. Canadian P. 262,194, 1926; *Chem. Abs.*, 1926, 20, 3581.

<sup>57</sup> A. Jäger, British P. 341,083, 1929, to Herold A.-G.; *Brit. Chem. Abs. B.*, 1931, 405.

<sup>58</sup> R. Hessen, British P. 159,461, 1921, to Bakelite G. m. b. H.; *J. S. C. I.*, 1922, 41, 771A.

<sup>59</sup> H. Lebach, British P. 27,096, 1908, to Knoll & Co.; *J. S. C. I.*, 1909, 28, 843. British P. 6430, 1911; *J. S. C. I.*, 1912, 31, 398.

<sup>60</sup> I. Eilersten, French P. 478,884, 1914; *J. S. C. I.*, 1916, 35, 1164.

the product with sodium carbonate solution. Final condensation was carried out after the addition of phosphoric acid, and a white translucent resin was formed. Similarly, Karsten<sup>61</sup> heated fusible soluble resins at 225-250°C. with boric acid or boric oxide. Bruhat<sup>62</sup> converted a liquid product prepared by the reaction of phenol, cresol or naphthols with anhydrous polymers of formaldehyde (paraformaldehyde, trioxymethylene) in the presence of traces of alkaline catalysts, into an insoluble infusible product by the addition of organic acids (lactic, acetic, formic, oxalic, tartaric, citric, gallic, tannic). Small amounts of mineral acids, hydrochloric, sulphuric, phosphoric and boric may also be present. The conversion takes place in the cold but more rapidly on heating. The initial liquid product with the acids added can be used as a varnish, or for gluing together laminae of wood, wood and fabric. Fillers, such as pumice, sand, glass, emery, asbestos, may be incorporated and the properties of the product may be varied by addition of gelatin, glue, naphthalene or rubber. Vessels resisting chemical reagents can be made from the final product. Thiele<sup>63</sup> performed the condensation of phenol and paraformaldehyde in two steps, as follows. In the first step a large excess of phenol was used, and the reaction was carried out at 80°C. A clear product was formed. To this was added more paraform, mixed with borax. The thick syrup which was obtained was converted into a solid resin by adding an excess of acid (hydrochloric, boric, tartaric, ammonium chloride), and heating at 100°C. for several hours.

Kulas and Pauling<sup>64</sup> proposed a two-stage process for preparing phenol-formaldehyde resin employing an acid catalyst (hydrochloric acid) in the first stage and an excess of base (caustic soda) in the second stage.

The amount of base considerably exceeds 10 per cent (by weight) of the quantity of phenolic body, and is more than sufficient to neutralize all of the acid catalyst. As an example, 50 parts of phenols, 25 parts of 40 per cent formaldehyde solution and 15 parts hydrochloric acid (sp gr 1.15) were boiled together for about 10-15 minutes. To the resulting mass 120 parts phenol, 90 parts 40 per cent formaldehyde, 10 parts ammonia and 2.5 parts sodium hydroxide were added. The mixture was heated under reflux for about 30 minutes. After removal of water a resin which could be thermally hardened was formed.

Instead of employing acid catalysts merely for polymerizing initial condensation products made by the use of alkaline catalysts, many investigators have chosen to carry out the entire condensation with acid catalysts. In the preparation of Novolak, it was found that maximum color stability was attained by the use of a small amount of phosphoric acid,<sup>65</sup> although hydrochloric<sup>66</sup> acid is the catalyst commonly used. Weak acids such as hydrogen sulphide, carbon dioxide or sulphur dioxide have been investigated as catalysts. An addition compound,  $H_2S \cdot 2CH_2O$ , is capable of reacting with phenol<sup>67</sup> to give a resin. Heinemann, Harvey and Robinson<sup>68</sup> heated phenols or cresols and formaldehyde or its polymers first without a condensing agent to yield liquid hydroxybenzyl alcohol, and this product was heated in an open vessel with sulphur dioxide solution. The product can be rendered insoluble by further heating or treatment with basic catalysts. Heinemann<sup>69</sup> obtained condensation products from phenols or cresols and formalde-

<sup>61</sup> E. Karsten, German P. 537,367, 1928; *Chem. Abs.*, 1932, 26, 1144.

<sup>62</sup> J. Bruhat, British P. 129,993, 1919; *Chem. Abs.*, 1919, 13, 2984.

<sup>63</sup> M. Thiele, German P. 289,565, 1916; *Chem. Abs.*, 1916, 10, 2626.

<sup>64</sup> C. Kulas and C. Pauling, U. S. P. 1,414,139, Apr. 25, 1922; *Chem. Abs.*, 1922, 16, 2234. See also Chapter 17.

<sup>65</sup> B. B. Mashkilleison and S. S. Zimmerman, *Plantische Massau*, 1932, 1, 32; *Chem. Abs.*, 1933, 27, 4426.

<sup>66</sup> L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, 1925, 17, 225.

<sup>67</sup> J. Lichtenberger, French P. 764,824, 1934, to Établissements Lambiotte Frères; *Chem. Abs.*, 1934, 28, 6004.

<sup>68</sup> A. Heinemann, H. C. Harvey and H. W. Robinson, British P. 28,187, 1914; *Chem. Abs.*, 1916, 10, 124.

<sup>69</sup> A. Heinemann, British P. 9390, 1914; *Chem. Abs.*, 1915, 9, 2801.

hyde by passing sulphur dioxide into the mixture of reactants, or the hydroxybenzyl alcohol made from them, and allowing the reaction to proceed without the application of external heat. The process was carried out in the absence of a solvent. According to Sarason,<sup>70</sup> condensation of phenols with formaldehyde proceeds more smoothly with sulphur dioxide as a catalyst than when strong acids are used. The products are alkali-soluble.

McCoy<sup>71</sup> effected the condensation in the presence of carbon dioxide. The reaction was interrupted when the product had become infusible and insoluble but was still capable of being softened by heat. After shaping, the material was further heated. Conducting the process in an atmosphere of carbon dioxide served to obviate the use of any other condensing agent. McCoy also proposed to obtain formaldehyde by the reduction of carbon dioxide with palladium hydride and permit the formaldehyde thus obtained to react in the presence of carbon dioxide as a condensing agent to produce resins. The palladium hydride could be regenerated by warming in a current of hydrogen gas. The process was carried out by passing carbon dioxide into a vessel containing the hydride suspended in water. Only a part of the carbon dioxide was reduced. The mixture of carbon dioxide and formaldehyde was passed into a second vessel containing phenol or cresol.<sup>72</sup> It has also been proposed<sup>73</sup> to condense phenol and formaldehyde by adding formic acid to the mixture, and heating under reflux for 1-2 hours. The viscous product was poured into molds and hardened first at 70-90°C., then, finally at 100-130°C.

Various strong acids besides hydrochloric have been found applicable in condensing phenols with formaldehyde. Birkby<sup>74</sup> used dilute sulphuric acid in the proportions of 500 volumes of phenol or its homologues, 450-550 volumes of 40 per cent formaldehyde, and 2-6 per cent by volume (relative to the volume of phenol) of dilute sulphuric acid. The latter was prepared by mixing 20 volumes of acid of 1.84 specific gravity with 80 volumes of water. The resinification was effected at a temperature of 60-80°C. After reaction and removal of water, the mixture was neutralized by milk of lime and the remaining water removed by heating *in vacuo*. The product could be finally hardened by heating under pressure. Melamid<sup>75</sup> also recommended dilute sulphuric acid as a phenol-aldehyde catalyst. Aylsworth<sup>76</sup> resinified phenol with a formaldehyde solution or with paraform, in proportions suitable to form an infusible product in the presence of sulphuric acid. When the reaction was partially complete a substance, such as barium carbonate, capable of forming an insoluble, electrically insulating salt with the mineral acid, was added, the quantity used being at least sufficient to combine with the whole of the acid present in the mass. Brunner<sup>77</sup> employed dry hydrogen chloride (see Chapter 17), and the resinous products were found to contain substituted chlorine.

It is possible to carry out the initial phase of the condensation of phenol with aldehydes in the presence of two catalysts, a mineral acid and a fatty acid. The mineral acid can then be removed, and the remainder of the condensation is catalyzed by the fatty acid alone.<sup>78</sup>

Alkyd resins<sup>79</sup> (see Chapters 41-49) have been proposed as catalysts for phenol-formaldehyde resins. A hardenable resin is made by reacting 1 mol of phenol, more than 1 mol of formaldehyde and 0.01-0.15 mol of an alkyd resin having an

<sup>70</sup> L. Sarason, German P. 219,570, 1908; *J.S.C.I.*, 1910, 29, 410.

<sup>71</sup> J. P. A. McCoy, U. S. P. 1,253,261 and 1,253,262, Jan. 15, 1918; *Chem. Abs.*, 1918, 12, 749.

<sup>72</sup> J. P. A. McCoy, U. S. P. 1,253,404, Jan. 15, 1918; *Chem. Abs.*, 1918, 12, 770.

<sup>73</sup> O. A. Cherry, U. S. P. 1,737,917, Dec. 3, 1929; *Chem. Abs.*, 1930, 24, 930.

<sup>74</sup> A. T. Birkby and F. E. Birkby, British P. 153,494, 1920; *Chem. Abs.*, 1921, 15, 1060. *Chem. Met. Eng.*, 1921, 28, 532.

<sup>75</sup> M. Melamid, U. S. P. 1,727,076, Sept. 3, 1929; *Chem. Abs.*, 1929, 23, 5283.

<sup>76</sup> J. W. Aylsworth, U. S. P. 1,197,171, Sept. 5, 1916; *J.S.C.I.*, 1916, 35, 1071.

<sup>77</sup> A. Brunner, German P. 550,326, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4065.

<sup>78</sup> G. S. Petrov and A. A. Pichuzina, Russian P. 31,615, 1933; *Chem. Abs.*, 1934, 28, 3254.

<sup>79</sup> French P. 768,031, July 30, 1934, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1935, 29, 524.

acid number of 140-210. The alkyd resin is preferably in the C stage and the resinifying reaction carried out at temperatures not above 130°C.

#### SULPHONATED COMPOUNDS

Sulphonated phenol-formaldehyde resins are discussed in Chapter 20. The present section is concerned with the use of various sulphonated derivatives as catalysts. During the early years of the World War a group of resins termed "Carbolites" was developed in Russia. Essentially, many of these were phenol-formaldehyde resins prepared in the presence of various quantities of sulphonated mineral oil. The amount of the latter in the final product was usually from 0-15 per cent (based on the formula  $C_{20}H_{27}SO_3H$ ) of the total. A typical procedure<sup>80</sup> was as follows:

One hundred parts of phenol, 30 parts sulphonated naphtha and 38 parts of 34 per cent formaldehyde solution were heated together, and the initial condensation product was separated from the water formed. Additional formaldehyde was then introduced in quantity sufficient to bring the total formaldehyde content (calculated as absolute  $CH_2O$ ) up to about 1/3 of the total phenol content. The material was placed in molds and hardened at 95-100°C. The sulphonated naphtha used as catalyst was not a pure sulphonic acid, but contained, in some cases, only about 45 per cent sulphonic acid based on the formula  $C_{20}H_{27}SO_3H$ . The Carbolites are infusible and insoluble, and, accordingly, are different from the "syntans" described in Chapter 20.

The catalyst<sup>81</sup> used in the preparation of the Carbolites is prepared by treating dry petroleum distillate ( $d=0.883-0.898$ ,  $N_{16}=1.49-1.50$ , Engler viscosity at 50°C., 1.47-1.95) with 5 per cent oleum (27 per cent  $SO_3$ ), and permitting the mixture to stand for a day. Then the acid layer is run off, and the remaining oil is aerated.

Various modifying agents have been used in conjunction with the Carbolites. Thus, Petrov<sup>82</sup> mixed phenol with glycerol prior to condensation with formaldehyde in the presence of sulphonated fatty acids or naphtha sulphonic acids. (See also Chapter 20.) The initial product was washed with water, neutralized with alkali and heated with additional formaldehyde. After cooling, the resin was mixed with hydrochloric acid and cast into molds to be thermally hardened. The molded articles were said to possess good dielectric properties. The mechanical and chemical properties of the Carbolites seemed to be determined by the nature of the starting materials and the method of condensation. Acid condensing agents are reputed to yield resins of low resistance to chemical action.<sup>83</sup> Aniline, benzene, carbon disulphide, benzine, turpentine and sunflower oil have no effect on the Carbolites. Acetone makes them disintegrate into small insoluble flakes. Carbolites containing fatty acids are more highly resistant to nitric acid than the unmodified resins. Dilute sodium hydroxide solution attacks the Carbolites, but dissolves only a few per cent of the resin content.<sup>84</sup>

Tarasov and Shestakov<sup>85</sup> obtained infusible insoluble products by condensing phenols with formaldehyde in the presence of salts of sulphonic acids (naphtha sulphonic acids or the so-called sulpho-aromatic fatty acids which are formed

<sup>80</sup> G. S. Petrov, *Plastics*, 1926, 2, 391; *Chem. Abs.* 1927, 21, 1020. G. S. Petrov, *Trans. Karpov Inst. Chem.*, 1925, 4, 136; *Chem. Abs.*, 1926, 20, 2394.

<sup>81</sup> M. D. Tikh'ev and A. I. Dumsku, *Neftyanoe Khozyaistvo*, 1926, 11, 763; *Chem. Abs.*, 1928, 22, 3286.

<sup>82</sup> G. S. Petrov, German P. 407,002, 1922; *J.S.C.I.*, 1925, 44, 461B. G. S. Petrov, British P. 205,167, 1922; *Chem. Abs.*, 1924, 18, 911. G. S. Petrov and V. I. Lasev, Russian P. 5027, 1924; *Chem. Abs.*, 1929, 23, 1729. G. S. Petrov and K. I. Tarasov, Russian P. 5145, 1928; *Chem. Abs.*, 1929, 23, 1764.

<sup>83</sup> A. D. Sokolov, *Plasticheskie Massy*, 1933, 3, 1; *Brit. Chem. Abs.* B, 1934, 895.

<sup>84</sup> G. S. Petrov, *Kunststoffe*, 1926, 16, 251; 1927, 17, 65; *Chem. Abs.*, 1927, 21, 1892. P. A. Florenskii, *Trans. State Elec. Research Inst. (Moscow)*, 1928, 21, 1; *Chem. Abs.*, 1931, 25, 4979.

<sup>85</sup> K. Tarasov and P. Shestakov, U. S. P. 1,237,579, Aug. 21, 1917; *Chem. Abs.*, 1917, 11, 3102. British P. 102,635, 1916; *Chem. Abs.*, 1917, 11, 1028. K. Tarasov, U. S. P. 1,235,507, July 31, 1917; *Chem. Abs.*, 1917, 11, 2722.

by sulphonating mixtures of fatty oils or olein and unsaturated hydrocarbons). An acid which does not decompose such salts was also present.

For example, 300 parts by weight of cresol were gradually mixed with 135 parts of a 40 per cent solution of sodium salts of "naphtha sulpho-acids," 9 parts of hydrochloric acid (sp.gr. 1.14), and 150 parts of 40 per cent aqueous formaldehyde, and heated to 65-70°C. A resinous liquid mass separated with a watery layer on top. The latter was removed and the resinous mass heated until there was a loss of 70-75 parts by weight of the total reactants used. After cooling to 35-45°C., 120 parts by weight of aqueous 40 per cent formaldehyde were added and the whole mixed to a homogeneous mobile liquid, which was poured into molds, cooled, kept for 1 hour at 45°C., and finally heated to 100°C.

Other sulphonated compounds besides sulphonated petroleum have been investigated as phenol-formaldehyde condensation catalysts. Long ago it was shown<sup>90</sup> that a mixture of sodium sulphite, formaldehyde and  $\alpha$ -naphthol yielded a crystalline hydroxynaphthylmethylsulphonic acid, but no mention was made of resinous by-products. Transparent infusible resins have been made<sup>91</sup> by condensing phenol with formaldehyde in the presence of naphthalene- $\alpha$ -sulphonic acid. In this case, glycerol and fusel oil were also incorporated, and the product was dehydrated *in vacuo*.

Pollak<sup>92</sup> used crystallized phenol, 18.8 parts, paraformaldehyde, 8.73 parts, and an aqueous solution of p-phenolsulphonic acid, 0.04 part. The mixture was warmed on a water bath and after completion of the reaction, the product was poured into molds in which, at about 100°C., it became hard and insoluble. If oxidation of the surface of the product was to be avoided, the process could be carried out in an inert gas, e.g., nitrogen, hydrogen or carbon dioxide. Before the reaction was completed and while the product was still in a soluble form, fillers or modifying agents could be added (asbestos, graphite, sand, powdered metals, tar, resins, oils, colors, cellulose, acetyl cellulose).

A self-hardening composition has been prepared by refluxing a commercial solution of formaldehyde (25-175 parts) with a phenol (210 parts). After cooling and removal of water, furfural (140 parts) was added along with 20-30 per cent of asbestos filler and 1-30 per cent of a product obtained by mixing 70 parts of concentrated sulphuric acid with 30 parts of ethyl alcohol.<sup>93</sup>

### SALTS

When salts are used as catalysts in phenol-formaldehyde condensations, their function is usually to control the course of the reaction by determining the hydrogen ion concentration. Accordingly, a mixture of zinc chloride and hydrochloric acid catalyzes the formation of products which are similar to those obtained by the use of hydrochloric acid alone.<sup>94</sup> In general, it appears that the nature of the resinous product is determined by the concentration of hydrogen ion,<sup>95</sup> and is largely independent of other ions which may be present during the reaction. It was early noted by Claypoole<sup>96</sup> that the resins formed from phenol and formaldehyde in the presence of sodium carbonate or sodium cresylate resembled those obtained through the use of sodium hydroxide. Story<sup>97</sup> had recorded the fact

<sup>90</sup> German P. 87,335, 1896, to Faiblenfabr vorm. F. Bayer & Co.; *Chem. Zentr.*, 1896, 2, 612.

<sup>91</sup> A. Danilowitsch and G. S. Petrov, British P. 231,501, 1925; *Chem. Abs.*, 1925, 19, 3605.

<sup>92</sup> F. Pollak, U. S. P. 1,216,728, Feb. 20, 1917 and French P. 420,404, 1910; *Chem. Abs.*, 1917, 11, 1734.

<sup>93</sup> P. Knapp, U. S. P. 1,884,747, Oct. 25, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1221.

<sup>94</sup> H. Stephen, W. F. Short and G. Gladding, *J.C.S.*, 1920, 117, 510.

<sup>95</sup> N. N. Vorozhtzov and E. N. Yuringma, *Zhur. Obshchei Khim.*, *Khim. Ser.*, 1931, 1, 49; *Chem. Abs.*, 1931, 25, 4521.

<sup>96</sup> W. Claypoole, British P. 2122, 1908; *J.S.C.I.*, 1909, 28, 252.

<sup>97</sup> W. H. Story, French P. 353,995, 1905; *J.S.C.I.*, 1905, 24, 1081A.



that resins made in the presence of salts differed from those made in the absence of added catalysts in that the latter were transparent. These facts indicate that the degree of acidity or alkalinity is more important than any specific catalytic properties attributable to the salt itself. Sugimoto<sup>94</sup> noted that each of the different types of phenol-formaldehyde condensation products could be obtained through the use of hydrochloric acid as catalyst, provided conditions are carefully controlled. Measurement of hydrogen ion concentration is a convenient means of ascertaining whether or not conditions are proper for the desired type of resin formation. Thus, Jackson and Cameron<sup>95</sup> found that the initial stage of the condensation took place at a  $pH$  of 6.5-8.5. This  $pH$  was maintained by the use of (1) triethanolamine, (2) trisodium phosphate, (3) a mixture of trisodium phosphate and sodium hydroxide, (4) phthalic anhydride and sodium hydroxide, (5) sodium phthalate or (6) a mixture of borax and sodium hydroxide. Neutral inorganic salts are added to serve as anti-foaming agents. By buffering the reaction mixture in the manner indicated, a clear liquid resin was produced. It could be molded and cured at 85-125°C. Matsumoto<sup>96</sup> noted that each stage in the condensation of phenol and formaldehyde was associated with a certain optimum degree of acidity or alkalinity. He regarded the resin-forming process as taking place in 3 stages, viz, the initial condensation, the concentration of the products and the final hardening. The best results were obtained when sodium hydroxide and ammonia were used as condensing agent and hardening agent respectively. The condensation proceeded satisfactorily in the presence of sodium sulphite or sodium carbonate, but these salts were not suitable hardening agents.

Dior<sup>97</sup> chose as a catalyst the ammonium salt of a volatile acid, and carried out the condensation in the following manner. Formaldehyde (40 per cent), 3 gal., was added to commercial carboic acid, 5.5 gal., and ammonium bicarbonate, 6 lbs., in a steam-jacketed digester provided with a reflux condenser. The reaction began in the cold and was completed by heating to 50-100°C. for about  $\frac{3}{4}$ -1 hour. The apparatus was then cooled by passing water through the jacket. The upper aqueous layer was decanted, and the condensation product left for 2-3 hours, after which time it was partially dehydrated. Finally, the resin was heated at 110-120°C. *in vacuo* or under normal pressure until all traces of water and catalyst were removed. Jaloustre, Kheifetz and Warchavsky<sup>98</sup> produced an acid-resistant infusible resin by treating phenol with formaldehyde solution in the presence of sodium salicylate or ammonium thiocyanate, 5 per cent (of the weight of phenol) and sodium cyanide, 2 per cent. The liquid and soluble product was hardened by heating at 95-100°C. in an open vessel. Moss<sup>99</sup> reacted approximately equal molecular proportions of phenol and formaldehyde in the presence of dihydrogen phosphates. The reaction was initiated by the use of phosphoric acid, and then sufficient ammonium or sodium hydroxide was added to form the dihydrogen phosphate. Pale fusible resins which were soluble in acetone were obtained.

With respect to the use of sodium carbonate as a phenol-formaldehyde catalyst, certain points of interest may be mentioned. Lebach noted<sup>100</sup> that when this condensing agent was employed, carbon dioxide was expelled violently and the caustic alkali set free was effective in carrying out the condensation. An intermediate

<sup>94</sup> S. Sugimoto, *Report Osaka Ind. Research Lab. (Japan)*, 1925, 6 (5), 1; *Chem. Abs.*, 1926, 20, 2755.

<sup>95</sup> E. H. Jackson and H. J. Cameron, U. S. P. 1,919,163, July 18, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 4943. French P. 41,304, 1932, addn. to 707,433, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 27, 2831.

<sup>96</sup> G. Matsumoto, *J. Chem. Ind. Japan*, 1915, 18, 434; *Chem. Abs.*, 1915, 9, 2317.

<sup>97</sup> R. E. Dior, British P. 124,010, 1919; *J.S.C.I.*, 1919, 38, 330A.

<sup>98</sup> L. A. Jaloustre, Z. Kheifetz and M. Warchavsky, British P. 138,061 and 139,147, 1919; *J.S.C.I.*, 1921, 40, 122A.

<sup>99</sup> W. H. Moss and C. Dreyfus, British P. 296,674, 1928, to British Celanese, Ltd.; *Brit. Chem. Abs.* B, 1930, 470. W. H. Moss, U. S. P. 1,743,680, Jan. 14, 1930, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 1529.

<sup>100</sup> H. Lebach, *J.S.C.I.*, 1913, 32, 559.

formaldehyde-carbonic salt was assumed. The cresols condense satisfactorily with sodium carbonate, sodium alcoholate or sodium formate.<sup>101</sup> A mixture of sodium carbonate and water-glass was proposed by Regal.<sup>102</sup> He also recommended sodium aluminate, sodium zincate or aluminum acetate. Rolker used sodium carbonate enclosed in a small perforated aluminum container.<sup>103</sup> The container was suspended in the reaction mixture, and was withdrawn when a definite viscosity of the mixture was attained. In this way, the reaction could be arrested at any stage. Another suitable method of controlling the condensation when sodium carbonate was used as the catalyst was to add oxalic acid to the reaction mixture<sup>104</sup> before the gelation stage has been reached.

A phenol-formaldehyde resinous product<sup>105</sup> of low viscosity and high solubility was obtained by Actmeyer using sodium tungstate or a mixture of sodium tungstate and trisodium phosphate as catalyst. White condensation products resulted when the catalyst was a mixture consisting of a borate (ammonium or an alkali metal borate) and a salt of tin, titanium, antimony, magnesium or zinc.<sup>106</sup>

Condensation by the use of salts of aromatic hydroxy acids, such as hydroxybenzoic or tannic, has been proposed by Wennagel.<sup>107</sup> For example,<sup>108</sup> 100 parts of phenol, 80 parts of formaldehyde and 5-10 parts of a 50 per cent solution of sodium salicylate were mixed and heated until an exothermic reaction started. Upon completion of the reaction, the water contained in the initial materials was expelled by evaporation, and the mass heated in molds. The product at this stage was liquid, but when the molds had cooled to about 60-80°C. they could be opened, the resin being then thoroughly solidified. A period of 12 hours was sufficient for this operation. Salts of aliphatic hydroxy acids have also been employed as catalysts. La Croux<sup>109</sup> treated a phenol-formaldehyde mixture with calcium carbonate, and then neutralized the resulting product with lactic acid. Sodium thiosulphate was added to obtain white substances, highly resistant to alkalis. The addition of lithopone gave the resin an ivory, citric acid a mottled ivory and calcium chloride a mother-of-pearl appearance. Added lead salts rendered the resin impenetrable by X-rays. Titanium citrate, tartrate and lactate have been used as catalysts for the formation of phenol-formaldehyde resins.<sup>110</sup> Sato<sup>111</sup> prepared a liquid product from phenol and formaldehyde with sodium sulphide and 5 per cent of an hydroxy fatty acid, e.g., glycollic, malic, lactic, tartaric or citric acid.

Petrov<sup>112</sup> used salts of hydroxy acids in the following manner: The phenolic substance was heated under reduced pressure with only a portion of total quantity of formaldehyde necessary for the reaction. This was done in the presence of coal-tar or mineral oils, suggested proportions being 100 parts of phenol, 15 parts of coal-tar oil, 70 parts of 40 per cent aqueous formaldehyde, and 10 parts of barium phenolate in 10 parts of water. A thick, transparent substance was formed. This was heated at atmospheric pressure until the volatile matter was removed. Thirty parts of 40 per cent formaldehyde were mixed with 100 parts of the initial resin, the temperature being kept below

<sup>101</sup> W. T. Robinson-Bindley, A. W. Weller and E. Duleken, British P. 145,128, 1919; *Chem. Abs.*, 1920, 14, 3134.

<sup>102</sup> A. Regal, French P. 468,241, 1914; *J.S.C.I.*, 1914, 33, 974. Dutch P. 2187, 1917; *Chem. Abs.*, 1918, 12, 412.

<sup>103</sup> E. Rolker, U. S. P. 1,532,952, April 7, 1925, to Permatite Co.; *Chem. Abs.*, 1925, 19, 1759.

<sup>104</sup> British P. 359,424, 1930, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 434.

<sup>105</sup> W. Actmeyer, U. S. P. 1,429,265, Sept. 19, 1922; Canadian P. 240,528, 1924; *Chem. Abs.*, 1924, 18, 2791.

<sup>106</sup> T. Akiyama and T. Sibuya, Japanese P. 89,615, 1930; *Chem. Abs.*, 1931, 25, 3136. Japanese P. 90,687, 1931; *Chem. Abs.*, 1931, 25, 4983.

<sup>107</sup> T. S. Wennagel, U. S. P. 1,273,967, July 30, 1918; *Chem. Abs.*, 1918, 12, 2046. French P. 483,915, 1917, to N. V. Hollandsche Proteïne Maatschappij; *Chem. Abs.*, 1918, 12, 983. Danish P. 21,606, 1916; *Chem. Abs.*, 1917, 11, 278.

<sup>108</sup> T. I. K. M. Hiltermann, British P. 117,857, 1917; *J.S.C.I.*, 1918, 37, 554A.

<sup>109</sup> G. A. La Croux, French P. 623,535, 1926; *Brit. Chem. Abs.*, B, 1930, 431.

<sup>110</sup> French P. 763,066, 1924, to Industrielle des vernis adhesifs; *Chem. Abs.*, 1934, 28, 5263.

<sup>111</sup> S. Sato, British P. 182,886, 1921; *J.S.C.I.*, 1922, 41, 676A.

<sup>112</sup> G. S. Petrov, British P. 205,167, 1922; *J.S.C.I.*, 1923, 42, 1243A.

50°C. At this point an emulsifying agent consisting of the potassium salt of an hydroxy acid made by oxidizing a drying oil was added in quantity up to 10-15 per cent. As an alternative this salt could be replaced by sulphonated castor oil. Upon removal of water a resinous product said to have good dielectric properties was obtained.

Considerable attention has been given to the use of alkali phenolates as catalysts for phenol-formaldehyde condensations. In a process<sup>113</sup> described by Brown and Kendall, trioxymethylene was dissolved in anhydrous cresol, and a wire cage containing balls of calcium cresolate was suspended in the mixture. An exothermic reaction was initiated by the application of moderate heat. An intermediate product was first formed, and this was converted to a hard resin by heating at 82-99°C. for five to six hours. Mellanoff<sup>114</sup> employed an alkaline solution of peat as a condensing agent. Also, phenols have been condensed with formaldehyde in the presence of powdered lead or zinc.<sup>115</sup> Petrov prepared a condensation catalyst by concentrating phenolic solutions of alkaline earth metals in the presence of a small quantity of formaldehyde.<sup>116</sup>

Wennagel<sup>117</sup> used soaps, particularly the resinate, stearate, palmitate and oleate of potassium, sodium, aluminum or calcium in quantities greater than one-fifth of the weight of phenol. The resins thus made are said to be more elastic than those made with more conventional catalysts. Sodium stearate and sodium sebacate were used by Jäger<sup>118</sup> as catalysts in the preparation of resins resembling horn.

Sodium sulphite was early investigated<sup>119</sup> as a catalyst in phenol-formaldehyde condensations. An addition compound of sulphite and formaldehyde was formed, and probably took part in the reaction mechanism. Robinson-Bindley, Weller and Dulcken<sup>120</sup> condensed formaldehyde, or substances yielding it, with o-, m- or p-cresol in the presence of sodium sulphite. The process was carried out by vaporizing the cresol with steam, and passing the vapors with formaldehyde into a reaction chamber containing sodium sulphite at a temperature of 60-90°C., or, alternatively, the cresol could be heated to 60°C. and formaldehyde gas blown through it in the presence of the catalyst. The product was further hardened by heating at 60-100°C. at atmospheric pressure or by heating it at higher temperatures under pressure. Scudder and Pettigrew<sup>121</sup> obtained a thin liquid phenolic condensation product, adapted for use in the preparation of impregnants, by allowing sodium sulphite, 40 per cent formaldehyde and carbolic acid, in about the proportions of 50, 100 and 1000 parts by weight respectively, to react together for 3 or 4 days with occasional stirring. The supernatant aqueous layer was removed, and the lower layer, containing 55-56 per cent of resin, could be used for impregnating porous articles, which were dried at 80-90°C. and heated under pressure for final hardening. Similarly, condensation products were prepared<sup>122</sup> by heating  $\beta$ -naphthol with an aqueous solution of formaldehyde in the presence of sulphites and sodium hydroxide. Byrom<sup>123</sup> has investigated the use of sodium

<sup>113</sup> K. Brown and D. S. Kendall, U. S. P. 1,263,031, Apr. 16, 1918, to Condensite Co.; *Chem. Abs.*, 1918, 12, 1590.

<sup>114</sup> I. S. Mellanoff, U. S. P. 1,681,155, Feb. 23, 1928, to Kemikal, Inc.; *Chem. Abs.*, 1928, 22, 3747. British P. 306,522, 1928, to Kemikal, Inc.; *Chem. Abs.*, 1929, 23, 5018.

<sup>115</sup> G. S. Petrov and P. Shestakov, U. S. P. 1,684,142, Sept. 11, 1928; *Chem. Abs.*, 1928, 22, 4213.

<sup>116</sup> A. K. Petrov and G. S. Petrov, Russian P. 4592, 1928; *Chem. Abs.*, 1929, 23, 1139.

<sup>117</sup> T. S. Wennagel, U. S. P. 1,107,003, Aug. 11, 1914.

<sup>118</sup> A. Jäger, British P. 281,537, 1927, to Herold A.-G.; *Brit. Chem. Abs. B*, 1928, 101. See also W. H. Story, British P. 8875, 1905; *J.S.C.I.*, 1906, 25, 195.

<sup>119</sup> H. Lebach, *J.S.C.I.*, 1913, 32, 559.

<sup>120</sup> W. T. Robinson-Bindley, A. W. Weller and E. Dulcken, British P. 134,564, 1918; *Chem. Abs.*, 1920, 14, 807.

<sup>121</sup> F. Scudder and R. Pettigrew, British P. 158,796, 1919; *J.S.C.I.*, 1921, 40, 19A. *Chem. Met. Eng.*, 1921, 26, 532.

<sup>122</sup> B. M. Lotarev, Russian P. 131, 1923; *Chem. Abs.*, 1933, 27, 4362.

<sup>123</sup> J. G. Byrom, U. S. P. 1,472,353, Oct. 30, 1923; *Chem. Abs.*, 1924, 18, 450. J. G. Byrom and R. Attwater, British P. 192,941, 1922; *Chem. Abs.*, 1923, 17, 3237.

thiosulphate in the manufacture of phenol-formaldehyde condensation products. A mixture of 112 lbs. of cresylic acid of 98 per cent purity and containing no sulphur compounds, 72 lbs. sodium thiosulphate and 16 lbs. of 40 per cent formaldehyde was heated to about 115°C. for 2 hours. Further quantities of 16 lbs. of 40 per cent formaldehyde were introduced at half-hour intervals until 64 lbs. had been added. As the condensation proceeded the product changed from a clear liquid to a plastic solid which was hardened by heating at 140-200°C.

Weindel<sup>124</sup> employed sodium hydrosulphite to restrain resinifications catalyzed by hydrochloric acid. Thus, 1000 parts phenol, 1000 parts 40 per cent aqueous formaldehyde and 10 parts hydrochloric acid of 24° Bé were heated together until a separation of oil occurred. Then 10 parts of sodium hydrosulphite were added, and the condensation was immediately arrested. The separated colorless oil thickened on cooling, forming a pasty plastic compound. To purify, the oil was stirred with cold or warm water, or steam was conducted into the mass. The product was soluble in alcohol and acetone and was proposed for use as a shellac substitute. In another example, twice as much hydrochloric acid was used, and, when the separation of oil had occurred, 17 parts of formaldehydesodiumsulphoxylate were added to arrest the reaction. On cooling, the condensation product was a white, opaque, plastic compound soluble in alcohol, acetone and ethyl acetate. When heated at 140°C. a resinous material was obtained. This was proposed for use as a shellac substitute. Smaller proportions of sodium hydrosulphite or formaldehydesodiumsulphoxylate gave insoluble products.

A large number of inorganic halides have been employed as phenol-formaldehyde catalysts. Zinc or aluminum chloride<sup>125</sup> gave a product which could be converted by means of acid into a resin said to be useful as a substitute for natural gums. Zirconium chloride also has been recommended.<sup>126</sup> Stockhausen and Grühl<sup>127</sup> kneaded a fluid phenolic condensation product at 30-50°C. with salts of trivalent metals (e.g., 50 per cent ferric chloride calculated on the phenol) and with sulphur, rubber or filling materials. After separation of water, the mass was heated and an infusible insoluble product was obtained. In preparing an initial condensation product the reaction could be interrupted at the point of incipient turbidity by sudden cooling. Plastic masses which were kneadable in the cold were made by condensing phenol with formaldehyde in the presence of alkaline earth chlorides, notably calcium chloride.<sup>128</sup> These plastics could be molded and thermally hardened. They were also adapted for incorporation in varnishes. When stannous chloride was used<sup>129</sup> as a condensing agent, the reaction was so energetic that it was necessary to cool the mixture at the beginning. No such reaction was noted when stannic chloride was used. Sato and Sekine<sup>130</sup> observed that copper carbonate, stannic chloride, ferric chloride and potassium ferrocyanide reacted with all types of phenol-formaldehyde resins. Color reactions were obtained with the insoluble infusible type. Schmidt<sup>131</sup> hardened the condensation products resulting from phenol-formaldehyde by treating with as small a quantity as possible of acid. Sufficient acid was provided by the hydrolysis of ethylenechlorohydrin or magnesium chloride. Plasticizers and clarifiers were also included in the final product, which was non-adhesive and suitable for cold-pressing

<sup>124</sup> A. Weindel, U. S. P. 1,039,850, Oct. 1, 1912; *Chem. Abs.*, 1912, 6, 3534.

<sup>125</sup> French P. 406,686, 1909, to Compagnie générale d'électricité; *J.S.C.I.*, 1910, 29, 577.

<sup>126</sup> P. Krishnamurti, *J. Madras Univ.*, 1928 Reprint; *Brit. Chem. Abs. B.*, 1929, 316.

<sup>127</sup> H. Stockhausen and R. Grühl, U. S. P. 1,150,642, Aug. 17, 1915; *Chem. Abs.*, 1915, 9, 2699. *British P.* 14,481, 1913; *J.S.C.I.*, 1914, 33, 799.

<sup>128</sup> German P. 481,207, 1922, to Société des verreries de Folembay; *Chem. Abs.*, 1929, 23, 5018. French P. 563,777, 1922, to Société des verreries de Folembay; *Brit. Chem. Abs. B.*, 1926, 955. *J. P. C. de Jarny*, U. S. P. 1,643,447, Sept. 27, 1927; *Chem. Abs.*, 1927, 21, 4035.

<sup>129</sup> G. W. Miles, U. S. P. 1,549,888, Aug. 18, 1925, to American Cellulose & Chemical Mfg. Co.; *J.S.C.I.*, 1925, 44, 837B.

<sup>130</sup> S. Sato and Y. Sekine, *J. Chem. Ind. Japan*, 1921, 24, 321; *Chem. Abs.*, 1922, 16, 1132.

<sup>131</sup> F. Schmidt, *British P.* 304,648, 1928; *Chem. Abs.*, 1929, 23, 4837. *British P.* 316,858, 1928; *Chem. Abs.*, 1930, 24, 1997. French P. 664,445, 1928; *Chem. Abs.*, 1930, 24, 981.

followed by thermal hardening. Weindel<sup>132</sup> similarly catalyzed phenol-formaldehyde condensations by means of chlorohydrins. Mannesmann<sup>133</sup> proposed sodium bromide or potassium bromide as catalysts for the condensation of cresol with formaldehyde. Sato<sup>134</sup> used copper sulphate, nickel sulphate, zinc chloride and calcium chloride for the conversion of liquid condensation products into hardened resins. Sulphuryl chloride, sulphur chloride, phosphorus oxychloride, acetyl chloride and benzyl chloride have been suggested as condensation catalysts by Matheson.<sup>135</sup> Phosphorus pentachloride has also been recommended.<sup>136</sup> The products obtained by the action of sulphur chloride on fatty oils (factice) were used by Buser.<sup>137</sup>

Various investigators have prepared resins from phenol and formaldehyde by the use of ammonium chloride as catalyst. For instance, in a process described by Hutin and Dauphin<sup>138</sup> 1 part of formaldehyde was mixed with 1 part of phenol (crude, synthetic). To this mixture was added one-quarter part of the residue obtained in the manufacture of synthetic phenol, 0.5-1 part water and 0.1 part of ammonium chloride. The reaction mixture was allowed to stand for several hours. Fillers were then added and the product molded in a heated press.

A translucent resin said to be useful in the preparation of an odorless varnish was made by reacting phenol with formaldehyde in the presence of ammonia, sulphuric acid or triethanolamine and calcium bromide. The initial product was dissolved in alkali and then reprecipitated with acid. A resin which could be washed, dried and dissolved in varnish solvents was obtained.<sup>139</sup>

A number of salts other than those mentioned above have been used as catalysts for the phenol-formaldehyde condensation. For instance, an insoluble infusible resin of dark garnet color was made by the use of sodium cyanide<sup>140</sup> as condensing agent. Sodium cyanide forms an intermediate substance recalling the aldehyde-bisulphite compounds.<sup>141</sup> In the presence of lead acetate, condensation of phenol with formaldehyde leads to formation of Novolaks, as might be expected because of the acidic nature of the reaction mixture.<sup>142</sup> Metal carbides, silicides or phosphides have been used by Nuttall<sup>143</sup> to catalyze the final stages of the condensation. The initial stages were catalyzed by ammonium chloride, sodamide, metal alcoholates or the compounds of ammonia with zinc or calcium chloride.

#### HALOGENS, OZONE AND SIMILAR CATALYSTS

Chlorine has been used as a catalyst in phenol-formaldehyde condensations.<sup>144</sup> In one instance phenol was heated first with a portion of the required amount of formaldehyde in the presence of chlorine and then with the remainder of the formaldehyde in the presence of sodium nitrate. After the reaction stopped, a further heating to a temperature above 120°C. followed. For example, formaldehyde (40 per cent solution), 34 parts, and crystallized phenol, 46 parts, were allowed to condense at 45-55°C. with 0.8 part of chlorine, and when the liquid be-

<sup>132</sup> A. Weindel, U. S. P. 1,039,859, Oct. 1, 1912; *Chem. Abs.*, 1912, 6, 3534.

<sup>133</sup> R. Mannesmann, Swiss P. 87,046, 1920; *Kunststoffe*, 1921, 11, 71.

<sup>134</sup> S. Sato, Japanese P. 39,329, 1921; *Chem. Abs.*, 1922, 16, 2761.

<sup>135</sup> H. W. Matheson, U. S. P. 1,653,302, Dec. 20, 1927; *Chem. Abs.*, 1928, 22, 849.

<sup>136</sup> E. Ropp, French P. 564,575, 1922; *Brit. Chem. Abs.* B, 1926, 955.

<sup>137</sup> J. J. Buser, German P. 273,192, 1913; *Chem. Abs.*, 1914, 8, 2817.

<sup>138</sup> A. J. B. Hutin and P. Dauphin, French P. 491,264, 1918.

<sup>139</sup> French P. 737,301, 1932, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 27, 1531.

<sup>140</sup> L. H. Buckeland, British P. 21,556, 1908; *J.S.C.I.*, 1909, 28, 374. L. A. Jaloustre, Z. Kheifetz and M. Warchavsky, British P. 138,061, 1921.

<sup>141</sup> L. H. Buckeland and H. L. Bender, *Ind. Eng. Chem.*, 1925, 17, 225.

<sup>142</sup> G. S. Petrov, German P. 442,211, 1921; *Brit. Chem. Abs.* B, 1928, 165. Russian P. 362, 1930; *Chem. Abs.*, 1933, 27, 4362.

<sup>143</sup> W. H. Nuttall, British P. 154,656, 1919, to Ioco Rubber & Waterproofing Co.; *J.S.C.I.*, 1921, 40, 91A. *Chem. Met. Eng.*, 1921, 24, 796.

<sup>144</sup> German P. 273,261, 1912, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1914, 8, 2817.

came somewhat gelatinous, 20 parts of formaldehyde solution and 0.5 part of sodium nitrate were added. After several hours the temperature was increased gradually to 70-80°C. until a viscous transparent strongly glutinous product was obtained. The completely dried product was reddish brown. By heating to over 120°C. it became infusible. Petrov<sup>145</sup> employed the sodium salt of toluenesulphonchloramide (Chloramine T) in catalyzing phenolic condensations. A mixture of 100 parts of phenol, 100 parts 40 per cent formalin and 2 parts toluenesulphonchloramide was heated until a viscous varnish-like mass separated. This material was soluble in varnish solvents and could be converted into an insoluble infusible resin by the application of heat.

Ozone, sandarac ozonide and pinene ozonide were found to catalyze the formation of phenol-aldehyde condensation products.<sup>146</sup> The decomposition products of ozonides also serve this purpose.<sup>147</sup> Ozonized formaldehyde likewise may be used,<sup>148</sup> the condensation being of the type taking place in the presence of acids. Phenolic resins are polymerized by the action of long wave-length radiations obtained from mercury vapor lamps.<sup>149</sup>

Seebach<sup>150</sup> found that Novolaks could be hardened by treating them with chloranil,  $C_6Cl_4O_2$ , or with a quinone. For instance, he mixed 90 parts Novolak, 10 parts quinone and 100 parts filler in a ball-mill. No volatile substances were formed, a circumstance which was quoted as an advantage possessed by this type of hardening agent.

<sup>145</sup> G. S. Petrov, U. S. P. 1,693,461, Nov. 27, 1928; *Chem Abs*, 1929, 23, 678 British P 283,002, 1927; *Brit Chem. Abs. B*, 1928, 164

<sup>146</sup> J. Kostal and J. Novak, British P. 227,468, 1924, to Regal & Co.; *Chem Abs*, 1925, 19, 2752 J. Novak and J. Kostal, Austrian P. 100,295, 1924 Czechoslovakian P. 15,438, 1924.

<sup>147</sup> A. Regal, Canadian P. 262,136, 1926; *Chem Abs*, 1926, 20, 3581.

<sup>148</sup> J. Novak and V. Cech, *Ind. Eng. Chem.*, 1928, 20, 796; 1932, 24, 1275.

<sup>149</sup> H. Steinmann, French P. 646,529, 1927; *Chem. Abs*, 1929, 23, 2309.

<sup>150</sup> F. Seebach, U. S. P. 1,893,415, Oct. 18, 1932, to Bakelite G m b H, *Chem Abs*, 1933, 27, 1113

## Chapter 17

### Phenol-Aldehyde Resins

#### V. Employment of Other Phenols

During the early growth of the phenol-aldehyde resin industry from 1907 to 1914, there was considerable restlessness, on the part of the limited number of manufacturers, with regard to phenol as a raw material. Commercially this feeling was justified. The world production of phenol was not large. Germany and England were the principal producers, and the only ones sufficiently large to export any. In the United States, production was very small and limited to a sole producer, whose product was used almost entirely for medicinal purposes. A certain amount was annually imported to provide the supply required in excess of domestic production. It is true that the potential production of this country was quite large, but it was scattered over a large area and the manufacturers were loath to compete with imported supplies.

There was a greater domestic production of cresols, and, moreover, these could be produced more cheaply. Speaking in relative terms phenol sold for 8 cents a pound, now and then on war scares and plagues or pestilence rising to 10 or 10½ cents. Cresylic acid, which was on the market, consisted of a mixture of the three isomeric cresols, ortho, meta and para, with small amounts of xylenols. In price it ranged from 5¼-8¼ cents per pound. The only difficulty was in the o-cresol content. That could be removed (at least, in part) by distillation<sup>1</sup> and used for disinfectant purposes. There was no sizeable production of other phenolic bodies. However, a great deal of experimental data on possible substitutes for coal-tar phenol were available.

The advent of the World War changed conditions materially. Imports of phenol were largely shut off and prices soared. The forehanded manufacturer, who had been able to lay in supplies, made large sums on the increase in value. Those with insufficient capital and poor sources of supply were very badly handicapped indeed. The production of synthetic phenol was commenced in this country, and though its first use was entirely for munitions purposes, its later developments had an important bearing on the resin industry. The tremendous demand for toluene expanded all phases of tar products recovery and supplies increased.

After the cessation of hostilities enormous supplies of unused phenol were on hand. Large plants for the production of synthetic phenol were idle and their owners had either to run them in competition with government-owned phenol, sold on a commission basis, or cease production. A few survived, and since that time there has always been an ample supply of relatively cheap phenol. Concurrently the expansion of the coal-tar industry has continued and the so-called natural phenols and cresols are in plentiful production.

<sup>1</sup> F. Ullmann, *Enzyklopädie der technischen Chemie*, Urban u. Schwarzenberg, Berlin, 1919, 7, 254. J. Scheiber, *Angew. Chem.*, 1933, 46, 503; *Chem. Abs.*, 1933, 27, 4975. H. Brückner, *Erdöl u. Teer*, 1928, 4, 580; *Chem. Abs.*, 1929, 23, 1246.

Shortly after this the early patents on Bakelite resins began to expire and the second era of the industry may be said to have begun. In this latter period the search has not been so much for cheaper replacements as for materials that would give different properties to the resultant resins.

#### RESINS FROM PHENOLIC TARs

Perhaps resins which occur during the coking of coal should be called natural resins. They do not occur in nature, as do the fossil resins, but they arise on treating coal with heat for the purpose of making coke. Trade custom has given the name of natural phenol to phenol extracted from coal-tar, in contrast to phenol made by sulphonation of benzene and fusion with caustic alkali, or by the more modern chlorination process. By analogy, resinous products from coal-tar are sometimes considered as natural resins.

In the past, when coking operations in this country were limited to city gas plants, coal-tar distillers concerned themselves largely in the production of creosote oils and pitch. Following the introduction of coke-ovens, an advance was made in that benzol began to be recovered. H. W. Jayne of Philadelphia, handicapped by unrestricted foreign competition, developed the production of benzene, toluene, xylene, naphthalene, phenol, cresol and other related chemicals.

As soon as tar began to be split into more than two simple components it was noticed that reddish resinous compounds could be obtained near the end of the distillation. These were collected and some attempts were made to study them. No published data of these studies exist, unfortunately. As the coal-tar industry grew, hard pitch at times accumulated to such an extent that attempts were made to subject it to further distillation to form pitch coke, a material in demand for the production of electrodes on account of its very low ash content. This further coking operation yielded considerable quantities of resinous bodies and at infrequent intervals they were studied in a desultory manner. Publication was again avoided and no results negative or otherwise are available.

Weiss<sup>a</sup> obtained by the destructive distillation of coal tar or coal-tar pitch a semisolid or solid bitumen stated to be suitable for waterproofing, molding, luting or use as a shoe filler. He also suggests mixing the bitumen with fibrous materials or other fillers and pigments. This same resinous material may be<sup>a</sup> incorporated with rubber to form electrical insulators or waterproofing compositions. A material proposed for use in paints or on roads is formed<sup>a</sup> when 80 parts of coal-tar pitch, 20 parts of petroleum naphtha and 1-3 parts of "tar acids" are mixed together. Resinous materials from coal tar according to Bailey and Boettner<sup>b</sup> may be employed, after purification by washing with 12 per cent of toluene, for mixing with other resins such as cumarone, indene or halowax resins, or such substances as sulphur, rosin, montan wax or carnauba wax. They may be used in varnish, rubber mixtures or waterproofing materials. The same investigators<sup>a</sup> proposed a waterproof composition to be made from "pitch resin" in the following proportions: resin 2.5, paraffin or wax 0.07, coal-tar naphtha 7.5 and high boiling tar acids 0.025 parts. They state that it is adapted to use on canvas or other fabrics.

Tars, because of their abundance and cheapness, their broad distribution, numerous points of production and usual phenolic content have been studied to a considerable extent as possible raw materials for resins of the phenol-aldehyde class. For such a use it is desirable that the properties and, if possible, the com-

<sup>a</sup> J. M. Weiss, U. S. P. 1,334,061, Mar. 16, 1919; *Chem. Abs.*, 1920, 14, 1434.

<sup>b</sup> J. M. Weiss, U. S. P. 1,334,060, Mar. 16, 1919; *Chem. Abs.*, 1920, 14, 1464. J. M. Weiss, U. S. P. 1,355,099, Oct. 5, 1920; *Chem. Abs.*, 1921, 15, 166.

<sup>c</sup> J. M. Weiss, U. S. P. 1,340,835, May 18, 1919; *Chem. Abs.*, 1920, 14, 2095.

<sup>d</sup> G. C. Bailey and F. Boettner, U. S. P. 1,355,103, Oct. 5, 1920; *Chem. Abs.*, 1921, 15, 166.

<sup>e</sup> G. C. Bailey and F. Boettner, U. S. P. 1,364,475, Jan. 4, 1921; *Chem. Abs.*, 1921, 15, 762.



position of the phenolic mixture be known. A great deal of work has been done on the composition of coal-tars,<sup>7</sup> and many methods have been worked out for the isolation or preparation of phenolic bodies from them. For example, p-xyleneol (2,4-dimethylphenol) can be obtained from the fraction boiling at 210-212°C. by treating the crude material with 0.2 part of sulphuric acid at 40°C. for 5 hours, and fractionally crystallizing the salt obtained by neutralization with ammonia. Hydrolysis of this salt gives p-xyleneol.<sup>8</sup> Among the compounds which have been obtained from coal-tar are phenol, the 3 cresols, 5 of the 6 xyleneols, 3-methyl-5-ethylphenol and 2,3,6-trimethylphenol.

Phenols of higher molecular weight than the xyleneols constitute approximately 66 per cent of the tar acids of low-temperature tar. The presence of aliphatic side-chains in these compounds is indicated by a decrease in specific gravity with increase in boiling point. As the boiling point rises further, this decrease in density gives way to a sharp increase, corresponding to the appearance of  $\alpha$ - and  $\beta$ -naphthols. Fractions of minimum density are collected at 234°C., and consist largely of 3-methyl-5-ethylphenol. Other simple alkylated phenols are collected up to 260°C.<sup>9</sup> In these compounds alkyl groups are located usually in the meta position to the hydroxyl. The chemical identity of many of the constituents<sup>10</sup> still remains in doubt. More subtle questions as to the nature of these materials are raised by the observation that intramolecular changes can occur between the hydrogen of a phenolic hydroxyl group, and various groups substituted in the ortho or para position.<sup>11</sup>

The use of tarry fractions for making phenol-formaldehyde resins usually involves some preliminary refining treatment. In the crude tars impurities are present which either catalytically affect the formation of resin, or give the product an objectionable texture. Ammonium salts and nitrogen bases are removed by washing the tar with water or dilute acid.<sup>12</sup> Sulphur compounds (mercaptans, thiophenols) and organic compounds of iron and aluminum are likewise objectionable, and are removable by fractional steam-distillation.<sup>13</sup>

Morgan carried out the purification and decolorization of phenols or neutral tar oils by heating them at 100°C. with 1 per cent formaldehyde in the presence of an acid or alkaline catalyst, and then distilling the product.<sup>14</sup> By treating acid tars at 80-160°C. under atmospheric or increased pressure<sup>15</sup> with aldehyde, and in the presence of phenols and condensing agents such as sulphuric or hydrochloric acid, it is possible to extract constituents with organic solvents, which are suitable for use in the manufacture of lacquers or plastic compositions. Sawdust can be added to the acid tar before reaction or it can be impregnated with the extracts of the condensation product, and mixed subsequently with the insoluble extraction residue. Karpati<sup>16</sup> devised a process for working up tar oils by converting the phenolic constituents into non-volatile condensation products by treat-

<sup>7</sup> G. T. Morgan, *Inst. Chem. Eng.*, 1933, 11, 17. G. T. Morgan, *J.S.C.I.*, 1932, 51, 67T. A. Brittain, F. M. Rowe and F. S. Sinnatt, *Fuel*, 1925, 4, 263, 299, 337; *J.S.C.I.*, 1925, 44, 796B. K. Ehrmann, *Brennstoff-Chem.*, 1929, 10, 405; *Brit. Chem. Abs. B*, 1929, 1003. G. T. Morgan and D. D. Pratt, *British P.* 318,116, 1928; *Brit. Chem. Abs. B*, 1929, 1006. Y. Postovskii and B. G. Perets, *J. Chem. Ind. (Moscow)*, 1928, 5, 635; *Chem. Abs.*, 1929, 23, 2026. E. B. Kester, *Ind. Eng. Chem.*, 1932, 24, 770. R. S. Andrews, *Proc. Soc. Chem. Ind. Victoria*, 1930, 30, 414; *Chem. Abs.*, 1931, 25, 1359. G. Vavon and N. Zaharia, *J. unives gaz*, 1928, 52, 534; *Chem. Abs.*, 1929, 23, 1247. J. J. Morgan and M. H. Meighan, *Ind. Eng. Chem.*, 1925, 17, 626. G. T. Morgan and A. E. J. Pettet, *J.C.S.*, 1934, 418. G. T. Morgan and A. E. J. Pettet, *J.S.C.I.*, 1935, 54, 19T.

<sup>8</sup> G. T. Morgan and A. E. J. Pettet, *British P.* 397,148, 1932; *Brit. Chem. Abs. B*, 1933, 907.

<sup>9</sup> S. Caplan, J. Ross, M. G. Sevag and T. M. Swits, *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 7.

<sup>10</sup> G. Dring, *J.S.C.I.*, 1933, 52, 963.

<sup>11</sup> J. B. Niederl and E. A. Sterch, *J.A.C.S.*, 1933, 55, 284. R. A. Smith, *J.A.C.S.*, 1934, 56, 717.

<sup>12</sup> S. P. Burke and M. R. Bhagwat, U. S. P. 1,911,745, May 30, 1933, to Combustion Utilities Corp.; *Chem. Abs.*, 1933, 27, 4111.

<sup>13</sup> V. Molinari, U. S. P. 1,909,848, May 16, 1933, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 3722.

<sup>14</sup> G. T. Morgan and A. E. J. Pettet, *British P.* 397,847, 1932; *Brit. Chem. Abs. B*, 1933, 951.

<sup>15</sup> German P. 354,539, 1919, to Plauson's Forschungsinat. G. m. b. H.; *J.S.C.I.*, 1922, 41, 863A.

<sup>16</sup> E. Karpati, *Chem. Rund. Mitteleuropa u. Balkan*, 1925, 2, 229; *Chem. Abs.*, 1926, 20, 2063.

ment with concentrated sulphuric acid or with formaldehyde. When concentrated sulphuric acid is used, residues capable of being used as tanning agents are obtained. Treatment with formaldehyde gives resinous condensation products of the phenol-aldehyde type. The neutral oil is separated from these by distillation in a current of superheated steam.

Another method<sup>17</sup> of getting rid of the neutral constituents of the coal-tar (b. p. up to 300°C.) before reaction with formaldehyde is to extract the tar with caustic alkali, and use the alkaline solution of phenolates for reaction with formalin or hexamethylenetetramine. The condensation is carried out at about 100°C. Excess alkali is neutralized with dilute sulphuric acid or by passing carbon dioxide (or flue gases) into the mixture. A granular resin is precipitated, and can be filtered, washed, dried, softened by heat, molded at high pressure and heat-hardened.

When the impurities in crude tar oil do not affect the rate of reaction of resin formation, but confer detrimental properties on the product, it is possible to treat the resin for the removal of undesirable constituents. A phenol-aldehyde resin is prepared by heating a coal tar fraction (b. p. 170-230°C.) with paraldehyde in the presence of pyridine, and extracting the product with warm benzene until the washings are colorless.<sup>18</sup> Final purification is accomplished by vacuum distillation with denatured alcohol. The paraldehyde may be replaced by formalin, pyridine by other bases and benzene by carbon tetrachloride or light oils.<sup>19</sup> The resins thus prepared were used in making single impregnated sheets and laminated boards, and the dielectric properties of the products were investigated. Resins from pure and crude phenol and two commercial resins were also tested for comparison. The tests showed that the mixed phenols of low-temperature tar are utilizable in the preparation of resins of high dielectric strength. The phenolic resins prepared as above have also been suggested for protecting wool against fungi<sup>20</sup> and for varnishes. Varnishes prepared from these resins darken on exposure but when mixed with aluminum powders, little darkening takes place. The tar resins furnish wood stains of even tone without raising the grain of the wood. It is customary to carry out the condensation of formaldehyde with phenolic tars in the presence of hydrocarbon oils, which occur in the tar or may be added to it for the purpose of thinning those already present. After the resin has formed, the mixture separates into three distinct layers, the main constituents of the several phases being, respectively, resin, water and hydrocarbon. Caplan<sup>21</sup> recovered the resins remaining in the hydrocarbon oil layer by adding a solvent for the oil in which the resinous condensation product is substantially insoluble, such solvents being petroleum ether, carbon tetrachloride or ether. Bhagwat<sup>22</sup> found that dilute mineral acid, such as hydrochloric or sulphuric acid, can be used to effect the separation. By shaking 1000 cc. of the hydrocarbon oil residue containing unrecovered resins with 150 cc. of 15 per cent hydrochloric acid, the resins separated as a deposit at the bottom, the purified oil collected in a layer at the top, while the acid solution remained in the middle layer.

The condensation of formaldehyde with phenolic tars can be carried out in the presence of a wide variety of catalysts other than those already mentioned. Tars were made more adaptable for road construction and roofing, according to Broad-

<sup>17</sup> M. R. Bhagwat, U. S. P. 1,948,465, Feb. 20, 1934, to Combustion Utilities Corp.; *Chem. Abs.*, 1934, 28, 2927.

<sup>18</sup> G. T. Morgan and N. J. L. Megson, *J.S.C.I.*, 1931, 50, 191T.

<sup>19</sup> G. T. Morgan, N. J. L. Megson and E. L. Holmes, *J.S.C.I.*, 1933, 52, 277T.

<sup>20</sup> G. T. Morgan, *J.S.C.I.*, 1932, 51, 67T.

<sup>21</sup> S. Caplan, U. S. P. 1,868,448, July 19, 1932, to Combustion Utilities Corp.; *Chem. Abs.*, 1932, 26, 5220. See also A. W. Luedcke, U. S. P. 1,985,453, Dec. 25, 1934, to Combustion Utilities Corp.; *Chem. Abs.*, 1935, 29, 1176.

<sup>22</sup> M. R. Bhagwat, U. S. P. 1,873,105, Aug. 23, 1932, to Combustion Utilities Corp.; *Chem. Abs.*, 1932, 26, 6166.

head and Andrews,<sup>23</sup> by heating in the presence of an aldehyde and a catalyst such as ammonia or ammonium sulphate to not over 100°C. in a closed vessel and then adding a catalyst such as ferrous sulphate and raising the temperature to 100-200°C. and passing air through the digested materials. Glud and Breuer<sup>24</sup> have made a study of the reaction between formaldehyde and various phenolic tars derived by low-temperature carbonization. Soluble, fusible resins were obtained from these phenols by treatment with formaldehyde using ammonium chloride as a catalyst. Crude tar oils containing phenols were condensed by heating with formaldehyde in the presence of such catalysts as sodium hydroxide, sulphuric acid, ammonia, ammonium chloride or benzylamine.<sup>25</sup> The resinous condensation products were separated from the neutral oil residue by steam distillation under reduced pressure. Hydrocarbons did not interfere with the resinification. Crude tar fractions boiling between 150-250°C. and also between 250-300°C. including the hydrocarbons that distil at these temperatures were used. Beutner and Hessen<sup>26</sup> treat phenolic tar oils (b. p. below 205°C.) with formaldehyde in the presence of alkaline condensing agents. Hydrocarbons or chlorinated hydrocarbons which are miscible with the neutral constituents of the tar, but which are not resin solvents, are added to assist the separation of the resin. Beutner<sup>27</sup> treated a coal-tar oil with formaldehyde, aqueous sodium hydroxide solution, and kerosene to yield a product which separates into three layers.

Thus, he heated 200 parts of 25 per cent tar acid oil, 40 parts of commercial kerosene, 80 parts of 40 per cent formaldehyde solution and 25 parts of a normal sodium hydroxide solution for ½ hour under reflux. After separation, the top layer consists of 190 parts of hydrocarbons, 85 parts of an aqueous layer are in the center and 75 parts of a resinous layer are at the bottom. The bottom layer can be heated to transform it into a soluble fusible resin or it can be heated beyond this to obtain an infusible insoluble resin. The condensation of a coal-tar oil distilling above 224°C. and preferably below 300°C. with aldehydes and ketones in the presence of alkaline catalysts has been investigated by Terwilliger.<sup>28</sup> For example, 100 parts of coal-tar oil boiling between 224 and 300°C., 30 parts of acetone, 50 parts of paraformaldehyde and 3 parts of sodium or potassium hydroxide are heated to effect condensation. The resin obtained may be used in a solvent as a baking varnish or it may be hardened by further heating to the infusible insoluble stage. Other ketones or other aldehydes (e.g., furfural) may be used.

Burke<sup>29</sup> produces a moldable and heat-hardenable synthetic resin by reacting a mixture of primary tar acids and unsaturated hydroaromatic hydrocarbons, with formaldehyde, in the presence of an alkaline condensing agent stronger than ammonia. One volume of 40 per cent formaldehyde solution, 3 volumes of tar oil (distilling 200-300°C.) and 2-10 per cent by weight of sodium carbonate solution are the proportions he suggests. The mixture, after heating and reacting until no tar acids remain in the oil, separates into layers, the fusible resin settling on the bottom.

<sup>23</sup> C. F. Broadhead and R. S. Andrews, Australian P. 17,101, 1928; *Chem. Abs.*, 1930, 24, 3341. R. S. Andrews, *Proc. Soc. Chem. Ind. Victoria*, 1930, 30, 414; *Chem. Abs.*, 1931, 25, 1359.

<sup>24</sup> W. Glud and P. K. Breuer, *Ges. Abhandl. Kenntnis Kohle*, 1919, 4, 221; *Chem. Abs.*, 1921, 15, 3550.

<sup>25</sup> French P. 607,655, 1925, to Comp. des mines de Vicoigne; *Brit. Chem. Abs. B*, 1927, 197.

<sup>26</sup> R. Beutner and R. Hessen, German P. 536,552, 1926, to August Nowack A.-G.; *Chem. Abs.*, 1932, 26, 1460. German P. 532,195, 1933; *Chem. Abs.*, 1934, 28, 919. For the production of drying and polymerizing oils from coal tar fractions by treatment with formaldehyde in the presence of a base see: J. J. Kessler, U. S. P. 1,616,321, Feb. 1, 1927; *Chem. Abs.*, 1927, 21, 1003. U. S. P. 1,739,597, Dec. 17, 1929; *Brit. Chem. Abs. B*, 1930, 318.

<sup>27</sup> R. Beutner, U. S. P. 1,653,281, Feb. 7, 1928, to August Nowack A.-G.; *Brit. Chem. Abs. B*, 1928, 308.

<sup>28</sup> C. O. Terwilliger, British P. 218,277, 1923 and 218,638, 1923; *Chem. Abs.*, 1925, 19, 581. Canadian P. 258,977, 1926; *Chem. Abs.*, 1926, 20, 2419. U. S. P. 1,624,082 and 1,624,638, April 12, 1927; *Chem. Abs.*, 1927, 21, 1990. Resinous products suitable for sound records are obtained by the action of aldehydes and ketones on coal-tar creosote. British P. 247,142, 1925, to Sild-Berliner Industrie Ges.

<sup>29</sup> S. P. Burke, U. S. P. 1,814,124, July 14, 1931, to Combustion Utilities Corp.; *Brit. Chem. Abs. B*, 1932, 518.

The rate of reaction of crude tar with formaldehyde in the presence of alkali is sometimes difficult to control, and accordingly there is danger of premature setting in the reaction kettle. One way of averting this is to neutralize the alkali in the reaction mixture at an early stage in the resin-forming reaction.<sup>30</sup> If lime is used as the alkaline condensing agent, neutralization with sulphuric acid is effected as soon as one mol of formaldehyde has combined with one mol of phenol. The precipitated calcium sulphate acts as a filler. Since the original catalyst has been rendered useless by the neutralization, it is thereafter necessary to substitute another catalyst, ammonia, by means of which the rate of resin formation can be controlled. Another method of controlling the reaction is to check the polymerization by the addition of alcohol or a mixture of alcohol and benzene soon after the initial condensation has taken place.<sup>31</sup> Caplan<sup>32</sup> employed the tar acid content of coal-tars for manufacture of a resin in the following manner.

A tar distillate comprising the entire fraction up to 300°C. was mixed with formaldehyde and a normal sodium hydroxide solution in the following proportions. 300 l. tar distillate (32 per cent tar acids by volume), 87.5 kg formalin and 20 l. sodium hydroxide. The mixture was heated in a kettle under a reflux condenser, agitated and maintained at a boil for 45 minutes. The heating was then discontinued and 600 l. of petroleum naphtha and 200 l. of water were added. The mixture was again agitated for a few minutes and then allowed to settle. Three sharply defined layers were formed. The bottom layer was withdrawn and heated rapidly under vacuum to a resinifying temperature, about 96°C. After occluded water and naphtha in the resin layer were distilled off, the temperature was allowed to rise to 105°C. and maintained there until the resin had suitably thickened. The product was drawn off and allowed to cool and harden. It was a potentially-reactive resin, capable of hardening when heated to 180°C. The purpose of the petroleum naphtha was stated to be for the prevention of portions of the resin remaining in the tar oil, either dissolved or suspended.

Resins prepared from the phenolic fraction of Baltic shale oil are described by Brodskii.<sup>33</sup> The best results were secured by reacting the phenols (derived by extraction of this fraction with a 10 per cent solution of sodium hydroxide) with formaldehyde. The fraction boiling between 170-320°C. can also be used directly but gives only a 25 per cent yield of resin. Artificial shellac or synthetic varnish resins are obtained by Harrison<sup>34</sup> by treating phenolic oils (obtained by destructive distillation of xanthorrhoea gum) with formaldehyde in the presence of an acid catalyst.

Gluud and Breuer<sup>35</sup> investigated the formation of resins not only from crude tar (*vide supra*) but also from a number of the phenolic compounds which can be obtained from this tar. Thus, cresols were treated with benzaldehyde in the presence of a small amount of ammonium chloride, the temperature being about 120°C., and the time of reaction 7 hours. The product was a thick viscous dark brown material which was soluble in alcohol and benzol. When heated at 170°C. under a pressure of 10 atmospheres a transparent dark-red hard resin resulted which, however, was easily fusible and was soluble in alcohol or aqueous alkali. In another experiment, 50 g. cresols, 66 g. paraldehyde and 2 g. ammonium chloride were heated several hours. Only 17 g. of a dark semi-solid mass, soluble in alcohol or benzene, was obtained. Soluble products also resulted when the phenols of low-temperature tar were condensed with formaldehyde. An investigation of vari-

<sup>30</sup> H. M. Dent, U. S. P. 1,894,088, Jan. 10, 1933, to General Plastics, Inc.; *Chem. Abs.*, 1933, 27, 2259

<sup>31</sup> E. S. Edwards, U. S. P. 1,970,649, Aug. 21, 1934, to Panelyte Corp.; *Chem. Abs.*, 1934, 28, 6329

<sup>32</sup> S. Caplan, U. S. P. 1,907,497, May 9, 1933, to Combustion Utilities Corp.; *Chem. Abs.*, 1933, 27, 3629

<sup>33</sup> G. S. Brodskii, *Plasticheskie Massy*, 1931, 1, 46; *Chem. Abs.*, 1932, 26, 3628.

<sup>34</sup> J. E. Harrison, Australian P. 14,531, 1928, to Black Boy Tanning & By-Products, Ltd.; *Chem. Abs.*, 1930, 24, 1529.

<sup>35</sup> W. Gluud and P. K. Breuer, *Ges. Abhandl. Kenntnis Kohle*, 1919, 4, 230; *Chem. Abs.*, 1921, 15, 3550.

ous types of phenolic bodies by carrying out condensation with formaldehyde in the presence of benzylamine was also made by Gluud and Breuer. In this case the reaction was carried to the final stage by heating under pressure in a "bakelizer" (see Fig. 57). In general the procedure employed was as follows.

Proportions of phenol and formaldehyde (30 per cent strength) to correspond to 1 mol each were mixed and heated to boiling under a reflux condenser. One-fifth of a mol of benzylamine was added and a violent reaction ensued. The heating was continued for 0.5-1.5 hours, then the reaction mass was cooled with ice and the aqueous layer removed. Exposure to the heat of the water bath caused the opaque resinous material to become clear. The heat treatment in the bakelizer consisted in exposing in an atmosphere of carbon dioxide at 100°C. under a pressure of 1.5 atmospheres. The carbon dioxide was allowed to flow through the bakelizer and the exit gases were noted to smell strongly of phenol. The temperature was gradually raised and at the end of one hour reached approximately 170°C. The carbon dioxide pressure was increased to 10 atmospheres, which pressure was maintained for 2 hours. Finally, the pressure was increased to about 15 atmospheres. When cold the products were very hard, clear, glass-like resins free from bubbles, infusible and insoluble in common solvents. They were found to be indifferent to alkalis and most acids.

Potentially reactive condensation products were made by Romieux<sup>36</sup> by reacting a mixture of phenols, boiling above 202°C., with formaldehyde in the presence of less than 0.1 per cent alkali based on the phenol present. One hundred parts of crude cresylic acid, boiling from 209-223°C., and 24.5 parts paraformaldehyde, or its equivalent of formaldehyde solution, are heated under reflux in the presence of 0.03 part of sodium hydroxide for 1.5 hours. The two layers are separated and the resinous portion is boiled to expel water and increase the viscosity. The resin can be hardened in a mold, or it may be mixed with fillers and molded. It is stated that molded objects made from this resin may be ejected from the press while still hot without danger of the surface blistering. Mursch<sup>37</sup> mixed dry fiber such as paper or rag material with cresylic acid, formaldehyde and caustic soda in the presence of water and boiled the mixture to form a doughlike plastic. Novak<sup>38</sup> prepared an impregnating compound by condensing cresylic acid with formaldehyde, in the presence of 1 mol of ammonia for every 4 mols of cresylic acid, mixing the condensation product with tung oil and heating the mixture until it was sufficiently clarified to remain limpid when cool. Any excess of the cresol is removed by adding hexamethylenetetramine or polymerized formaldehyde. Lignin cresol resins have been proposed for molding materials. Fischer, Horn and Küster suggested<sup>39</sup> replacing the lignin by lignite or lignitic brown coal. Pulverized lignite, vacuum dried, is kneaded at 80°C. with 12 per cent cresol in a volatile solvent, which is removed by vacuum distillation. At the end of the reaction the material is subjected to a pressure of 300 kg. per sq. cm. at 150°C. They state it is stable, odorless, nonmelting, and its raw materials cost 1/10 of the cost of phenol-formaldehyde ingredients. Molding compositions can be made by impregnating fillers with the condensation product obtained by treating an alkaline solution of peat with a mixture of formaldehyde and phenol.<sup>40</sup>

Coniferous wood tar, saponified with concentrated alkalis, separated from the unsaponifiable matter and warmed with formaldehyde yields a viscous product. This is separated from the aqueous portion, washed repeatedly with water and dried. A hard, transparent, brown resin is obtained which is soluble in naphtha,

<sup>36</sup> C. J. Romieux, U. S. P. 1,669,694, May 15, 1928, to American Cyanamid Co.; *Chem. Abs.*, 1928, 22, 2475.

<sup>37</sup> J. Mursch, U. S. P. 1,869,490 and 1,869,491, Aug. 2, 1931, to Joseph Gatti; *Chem. Abs.*, 1932, 26, 5440.

<sup>38</sup> I. J. Novak, British P. 334,232, 1929; *Chem. Abs.*, 1931, 25, 1045.

<sup>39</sup> F. Fischer, O. Horn and H. Küster, *Brennstoff-Chem.*, 1932, 13, 468; *Chem. Abs.*, 1933, 27, 2014.

<sup>40</sup> I. S. Mellanov, U. S. P. 1,857,090, May 10, 1932, to Kemikal, Inc.; *Brit. Chem. Abs. B*, 1933, 317. I. S. Mellanov, U. S. P. 1,681,155, Aug. 14, 1928; *Brit. Chem. Abs. B*, 1928, 866.

and the solution is used, mixed with mineral colors, as a paint.<sup>41</sup> Lingner<sup>42</sup> condensed "vegetable tar" with 40 per cent formaldehyde solution by the aid of hydrochloric or sulphuric acid. The resulting solid mass was dissolved in alkali and reprecipitated by dilute acids several times, then washed, dried and powdered. The product is claimed to possess all the medicinal properties of the original tar, but has the advantage of being practically odorless.

### CRESOLS AND XYLENOLS

In addition to the cresylic acids of commerce, which are usually mixtures of the three isomers, ortho, meta and para, there are fractions of tar acids containing substantial amounts of xyenols. These are known as high-boiling tar acids, or simply as H.B. Tar acid. Their main use is for the preparation of high-phenol-coefficient disinfectants, but they have attracted some attention as a source of phenol replacements. The melting and boiling points<sup>43</sup> of the cresols and xylenols and a few other homologues are given in Table 27.

TABLE 27—*Melting and Boiling Points of Various Phenols*

Type of Phenol		Melting Point	Boiling Point
Phenol		42.5°C.	181.5°C.
o-Cresol	2-methylphenol	30	190.8
m-Cresol	3-methylphenol	4	202.8
p-Cresol	4-methylphenol	36	201.5
2,3-Xylenol	2,3-dimethylphenol	75	218
2,4-Xylenol	2,4-dimethylphenol	26	211.5
2,5-Xylenol	2,5-dimethylphenol	74.5	211.5
2,6-Xylenol	2,6-dimethylphenol	49	212
3,4-Xylenol	3,4-dimethylphenol	65	225
3,5-Xylenol (symmetrical)	3,5-dimethylphenol	63.2	220.2
o-Ethylphenol	2-ethylphenol	-18	206.5-7.5
m-Ethylphenol	3-ethylphenol	-4	217
p-Ethylphenol	4-ethylphenol	46	218.5-9
Symmetrical methylethylphenol	3-methyl-5-ethylphenol	55	232.5-4.5
Isopseudocumenol	2,3,5-trimethylphenol	95-6	233
Mesitol	2,4,6-trimethylphenol	68-9	219.5
Pseudocumenol	2,4,5-trimethylphenol	71-2	234-5

The reactive positions in these compounds are ortho and para to the hydroxyl groups (see Chapter 14). Introduction of an alkyl group in the ortho position tends to reduce the reactivity of the para hydrogen, but meta substituting alkyl groups enhance this reactivity. The relative rates of condensation of substituted phenols with formaldehyde apparently parallel the reactivity series obtained by Hodgson and Jenkinson, who compared the rates at which various substituted phenols reacted in the Reimer-Tiemann reaction.<sup>44</sup> Symmetrical xylenol (3,5-dimethylphenol), which has three reactive hydrogens (2 ortho and 1 para) reacts with formaldehyde faster than phenol or m-cresol. It is of interest to note that m-cresol polymerizes with formaldehyde to a greater extent than does phenol.<sup>45</sup>

The rate of cure of resins made from cresols or xylenols is influenced by the

<sup>41</sup> German P. 338,554, 1919, to Chem. Fabr. Florsheim H. Noerdlinger; *J.S.C.I.*, 1921, 40, 742A. See also P. Bardy, French P. 402,907, 1908, to Pagès Camus et Cie; *J.S.C.I.*, 1909, 28, 1320.

<sup>42</sup> K. A. Lingner, French P. 329,971, 1903, *J.S.C.I.*, 1903, 22, 1014.

<sup>43</sup> Beilstein, "Handbuch der Organische Chemie," 4th Edition, VI. H. Bruchner, *Erdöl u. Teer*, 1928, 4, 562, 580, 598; *Chem. Abs.*, 1929, 23, 1246. O. Kruber and A. Schmitt, *Ber.*, 1931, 64, 2270. *Chem. Abs.*, 1932, 26, 113. F. Raschig, British P. 18,334, 1899; *J.S.C.I.*, 1900, 19, 37. British P. 25,269, 1899; *J.S.C.I.*, 1900, 19, 1099. F. Raschig, *Z. angew. Chem.*, 1900, 31, 759; *J.S.C.I.*, 1900, 19, 1099. E. B. Kester, *Ind. Eng. Chem.*, 1932, 24, 770.

<sup>44</sup> H. H. Hodgson and T. A. Jenkinson, *J.C.S.*, 1929, 469, 1641.

<sup>45</sup> H. Stäger, *Helv. Chim. Acta*, 1931, 14, 285; *Chem. Abs.*, 1931, 25, 3183. N. J. L. Megson and A. A. Drummond, *J.S.C.I.*, 1930, 49, 255. This subject is also considered in Chapter 16.

positions of the alkyl groups. Resins from o-cresol cure very slowly, and accordingly it is an undesirable constituent of resin-forming tars. o-Cresol may be detected by means of viscosity measurements.<sup>46</sup>

Though o-cresol has the disadvantage noted, uses for it in the preparation of resins have been proposed. To illustrate,<sup>47</sup> o-cresol was heated for several hours at 100°C. with formaldehyde, or substances capable of producing it, in the presence of acids, and the cooled mass was washed with water and purified by treatment with steam. The resultant product was a hard resin, varying in color from yellow to light brown, and melting at about 110-128°C. It was soluble in methyl and ethyl alcohols, dilute caustic alkali solutions, acetone, ether, carbon disulphide and chloroform; less soluble in benzol, chlorohydrin, carbon tetrachloride, turpentine oil and fatty oils. It served as a substitute for shellac and yielded varnishes which dry well on wood or metal. The hardness of the product depended upon the proportion of formaldehyde used. Ellis<sup>48</sup> described a composition containing an o-cresol-formaldehyde resin mixed with tung oil and asbestos. The particles of this mixture could be welded together by means of high pressure, without the application of heat. By condensing o-cresol (100 parts) and formaldehyde (70 parts 40 per cent solution) with acids (5 parts concentrated hydrochloric acid and 60 parts water), Gentsch<sup>49</sup> obtained straw yellow to light brown resins melting at 110-120°C. which were soluble in dilute alkalies, alcohol, acetone and chloroform. They were sparingly soluble in benzene and carbon tetrachloride, but insoluble in linseed oil and turpentine. Such resins, he states, furnish an odorless coating which dries well when used in varnishes or polishes.

Both o- and p-cresol tend to form permanently fusible and soluble resins of the saliretin type.<sup>50</sup> o-Cresol is considered particularly undesirable in making resins for molding compositions which have to be hardened in the mold. Baekeland, however, sought to utilize this relative inactivity in the production of resins which could be used as plasticizing agents. While it is true that infusible products may be obtained from o- and p-cresol, their production involves a length of heating which would be out of the question in any commercial molding operation requiring hot pressing. An infusible product may be prepared according to Baekeland when p-cresol reacts upon formaldehyde present in sufficient proportions, provided caustic soda is used as the condensing agent. If hydrochloric acid is used the product is more or less fusible and brittle. Similar proportions of formaldehyde reacting on phenol or m-cresol would result in infusible products. From o-cresol Baekeland has prepared a series of resins which are used to retard the time of final hardening in molding compositions made essentially from phenol or m-cresol and formaldehyde. He also described methods of making several varieties of infusible resin from o-cresol. A typical example is as follows:

One hundred g. o-cresol, 64 g. formaldehyde solution (40 per cent) and 1.6 cc. of concentrated hydrochloric acid were boiled for about 2 hours, then evaporated and heated to 200°C. A fusible resin of the saliretin type resulted. This was mixed with about 7-15 per cent by weight of paraform, and heated for 24-48 hours in a mold at a pressure of 45-90 lbs. The product was hard and infusible.

Aylsworth<sup>51</sup> prepared an oil-soluble cresol resin by heating together o-cresol, 30 parts, and a 40 per cent solution of formaldehyde, 14-16 parts, with a small amount of water. The water is not necessary but it decreases the violence of the

<sup>46</sup> J. Scheiber, *Angew. Chem.*, 1933, 46, 503; *Chem. Abs.*, 1933, 27, 4975.

<sup>47</sup> French P. 384,425, 1905, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1908, 27, 457.

<sup>48</sup> Carleton Ellis, U. S. P. 1,645,693, Oct. 18, 1927; *Chem. Abs.*, 1928, 22, 174.

<sup>49</sup> C. Gentsch, U. S. P. 924,440, June 8, 1909, to Farbenfabr. vorm. F. Bayer & Co.; *Chem. Abs.*, 1909, 3, 2242.

<sup>50</sup> L. H. Baekeland, U. S. P. 1,401,553, Jan. 3, 1922; *Chem. Abs.*, 1922, 16, 966. U. S. P. 1,306,681, June 17, 1919; *Chem. Abs.*, 1919, 13, 2264.

<sup>51</sup> J. W. Aylsworth, U. S. P. 1,111,287, Sept. 22, 1914; *Chem. Abs.*, 1914, 8, 3634.

reaction. The amount added may be as much as 8 parts. Heating is done in an autoclave at 130°C. Excess of cresol and water are removed by vacuum distillation. The resulting resin melts at 60-77°C., and contains under 4 per cent of cresol. The formaldehyde is all combined and the resin is soluble in varnish oils and solvents. Berend<sup>52</sup> produced soluble fusible resins insoluble in linseed oil by reacting crude cresol with sufficient formaldehyde to combine with the m-cresol. The uncombined cresols were recovered from the mixture by vacuum distillation. Robinson-Bindley, Weller and Dulcken<sup>53</sup> prepared an oil-soluble product by condensing 50 parts of p-cresol with 70 parts of 40 per cent formaldehyde solution. Five parts of hydrochloric acid of 30 per cent strength constituted the catalyst. Oil-soluble resinous condensation products also are obtained from phenolic lignite-tar oils or low-temperature coal-tar oils by condensation with not more than a molecular proportion of acetaldehyde or higher aldehydes. Mixtures of acetaldehyde and higher aldehydes likewise may be used.<sup>54</sup> The addition of these oil-soluble resins to phenol-formaldehyde resins which are insoluble in oil is stated to confer solubility upon the phenol-formaldehyde resins. Subsequent treatment of the oil-soluble resins with formaldehyde converts them into products which are insoluble in oil.<sup>55</sup> A comparison of the resin from pure m-cresol<sup>56</sup> with products made from mixtures of cresol isomers indicates that the presence of o- and p-cresol has a softening effect. It has been reported that the best results are obtained when the m-cresol content is 60-70 per cent.<sup>57</sup> By boiling commercial cresylic acid of 97-99 per cent purity with such a proportion of 40 per cent formaldehyde solution that the mixture contains more than one molecule of formaldehyde for each molecule of cresylic acid and continuing the boiling until the solids determined at a temperature of 110°C. equal at least 40 per cent of the product, Handy<sup>58</sup> produced a resin which was infusible, hard, tough and insoluble in acetone. The final boiling, during which water and formaldehyde are distilled off, was conducted at a temperature of 110-120°C. The product obtained by this method was reported to be suitable for use as a binder in making brushes and for various other purposes. Compositions for use in brake-linings may be made by reacting cresylic acid and not more than 58 per cent (based on cresylic acid) of a 40 per cent formaldehyde solution.<sup>59</sup> A paint or enamel is prepared by Ornstein<sup>60</sup> as follows:

A solution of cresol 100, sodium hydroxide 6, water 94 and 40 per cent formaldehyde 75, after standing 12 hours, is mixed with a 10 per cent hydrochloric acid solution 100 parts, and the product allowed to settle to obtain an oily layer. A second solution of cresol 100, sodium hydroxide 6, water 94 and 40 per cent formaldehyde 60 parts, is heated to boiling and 15 parts formaldehyde and a 10 per cent hydrochloric acid solution are added, also producing an oily layer. The two oils are mixed, and solvents and pigments added to form paints. A small quantity of a chloride, nitrate or sulphate may be added to promote hardening.

Transparent condensation products from a mixture of equimolecular quantities of purified cresol or phenol and 40 per cent aqueous formaldehyde with 0.5 per cent alkali hydroxide as catalyst are prepared by distilling off, under normal pressure, all the water used for solution and half the water formed in the con-

<sup>52</sup> L. Berend, U. S. P. 1,214,414, Jan. 30, 1917; *Chem. Abs.*, 1917, 11, 1320

<sup>53</sup> W. T. Robinson-Bindley, W. Weller and E. Dulcken, British P. 134,563, 1918; *J.S.C.I.*, 1920, 39, 35A.

<sup>54</sup> British P. 156,740, 1921, to Chem. Fabr. Worms Akt.-Ges.; *Chem. Abs.*, 1921, 15, 1821.

<sup>55</sup> Concerning the effect of natural resins in conferring solubility in oil, see Chapter 19.

<sup>56</sup> L. H. Baekeland, U. S. P. 1,038,677 and 1,038,678, March 3, 1914, to General Bakelite Co.; *J.S.C.I.*, 1914, 33, 430

<sup>57</sup> T. Shono, *J.S.C.I. (Japan)*, 1920, 33, 24B; *Chem. Abs.*, 1920, 24, 1905.

<sup>58</sup> J. O. Handy, U. S. P. 1,237,299, Dec. 10, 1918, to Pittsburgh Testing Laboratory; *Chem. Abs.*, 1919, 13, 369. For a discussion of cresylic acid resins, see: Wm. McHutchison, *Ind. Chemist*, 1934, 10, 383.

<sup>59</sup> Wm. Nanfeldt, U. S. P. 1,980,221, Nov. 13, 1934, to World Bestos Corp.; *Chem. Abs.*, 1935, 29, 257.

<sup>60</sup> L. S. Ornstein, U. S. P. 1,222,980, Apr. 17, 1917; *Chem. Abs.*, 1917, 11, 1912.



densation. The residue is mixed with 20 volumes (of the original volume) of methyl or ethyl alcohol, and then half the alcohol distilled off. Subsequently the residue is poured into molds and dried in a chamber through which a current of air is passed. The drying is begun at 60°C. and the temperature is gradually increased to 115-120°C. or higher. A hardened and nonfusible product is formed.<sup>61</sup> One mol of cresol may be condensed with 2 mols of formaldehyde in the presence of triethanolamine, urea and guanidine carbonate. Potassium bromide is added as a dispersing agent. The product is thermally hardened.<sup>62</sup> Cresols are condensed, according to Chestakoff,<sup>63</sup> with formaldehyde in the presence of catalysts of low activity such as oxalic acid, succinic acid, zinc or lead acetate. Material thus obtained is suitable for casting in molds. For this purpose it is mixed with organic monosulphonic acids of high molecular weight readily soluble in the material and is heated for 5-10 hours at 110-130°C. Mathieu<sup>64</sup> uses equal volumes of cresol and 40 per cent formaldehyde solution and condenses the mixture in the presence of acids such as hydrochloric, sulphuric or oxalic, at 65-72°C., until the product solidifies on cooling. The resin is suggested for molding or for mixing with rubber prior to vulcanizing.

Mannesmann<sup>65</sup> obtained a product resembling shellac by condensing cresol and formaldehyde in the presence of halogenated hydrocarbons. The preparation of a resin from hexamethylenetetramine and a rather large proportion of cresol is accomplished by heating a mixture of 1080 lbs. cresol and 140 lbs. hexamethylenetetramine to a temperature of 140°C. After the rapid evolution of ammonia ceases, heating is continued at a temperature of 165°C. for 48 hours, and hot air is blown through the mass to drive off the unreacted cresol. Seventy-eight lbs. of creosote oil (b. p. 220-270°C.) are then mixed into the product at a temperature of 85-125°. Following this, an additional 120 lbs. of hexamethylenetetramine are introduced. The product is a potentially reactive resin, which can be mixed with fillers, pulverized, molded and thermally hardened.<sup>66</sup> From a fraction consisting of a mixture of cresols and xyenols, Mains<sup>67</sup> obtained condensation products with aldehydes, using alkaline catalysts (see also Chapter 24). One hundred and twenty-five parts, for example, of a coal-tar acid containing 75 per cent m- and p-cresols and about 25 per cent xylenols, 96 parts of furfural and 1 part of sodium carbonate are boiled under reflux for 3-4 hours with stirring. The excess water and furfural are distilled off and a dark reddish-brown resin, soluble in acetone, furfural, mixtures of benzene and alcohol and other organic solvents, is obtained. Formaldehyde solution may be used in place of the furfural and by adding small percentages, from 1-10 per cent, of paraform, furfuramide, or hexamethylenetetramine, the resin is converted into a potentially reactive product. Kulas and Pauling<sup>68</sup> heated xylenol with formaldehyde in the presence of an acid catalyst until resin formation had taken place. The hot resin was mixed with more xylenol and formaldehyde and a sufficient quantity of a basic catalyst to leave an excess of alkali in the product. Prolonged heating caused the final hardening of the resin.

A xylenitic resin which has the property of softening but not flowing when placed upon a hot plate, and which sets when subjected to hot-pressing at a tem-

<sup>61</sup> Dutch P. 3,742, Sept. 15, 1919, to N. V. Utrechtsche Chemische Industrie; *Chem. Abs.*, 1922, 16, 2971.

<sup>62</sup> H. J. Cameron and E. H. Jackson, British P. 364,064, 1930, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1932, 272.

<sup>63</sup> P. Chestakoff, French P. 659,695, 1927. British P. 303,022, 1928; *Chem. Abs.*, 1929, 23, 5283.

<sup>64</sup> E. Mathieu, French P. 673,242, 1929; *Chem. Abs.*, 1930, 24, 2558.

<sup>65</sup> R. Mannesmann, Danish P. 24,697, 1919; *Chem. Abs.*, 1920, 14, 1227.

<sup>66</sup> L. V. Redman, A. J. Weith and F. P. Brock, U. S. P. 1,242,592, Oct. 9, 1917, to Redmanol Chem. Prod. Co.; *Chem. Abs.*, 1918, 12, 209.

<sup>67</sup> G. H. Mains, U. S. P. 1,835,610, Dec. 8, 1931, to Westinghouse Electric & Mfg. Co.; *Chem. Abs.*, 1932, 26, 1144. U. S. P. 1,976,572, Oct. 9, 1934; *Chem. Abs.*, 1934, 28, 7564.

<sup>68</sup> C. Kulas and C. Pauling, Swiss P. 100 402, 1922.

perature of 165°C., has been prepared by Ellis<sup>66</sup> as follows: 30 parts by weight of magnesium oxide are ground with 150 parts of aqueous 40 per cent formaldehyde solution and the mixture is added to 122 parts of xyenols (b. p. 200-225°C.). The batch is agitated at 70°C. for about 25 minutes, at the end of which time the formaldehyde has been entirely consumed. After drying *in vacuo* at 72°C., the light yellow resin, which resembles sulphur in appearance, is mixed in a pebble mill with an equal weight of wood flour. One per cent aluminum palmitate may be added if the resin is to be molded. Drummond and Morgan<sup>70</sup> condensed xylenols distilling between 215-224°C. with formaldehyde in the presence of an acid catalyst. The products are soluble in alcohols, ketones, hydrocarbons and fatty acid esters; they may be used for making air-drying varnishes by heating at 170°C. for 1-2 hours with a drying oil. Synthetic resins are produced by Anderson and MacLaurin<sup>71</sup> through the condensation of formaldehyde with monohydric phenolic substances, boiling between 230-320°C., present in tars obtained by the low temperature distillation of coal. A process of condensing xylenols with formaldehyde to produce resins is given by Landt.<sup>72</sup> The proportions used are, 100 parts of the xyleneol or mixture of xyleneols, 60 parts of 40 per cent formaldehyde solution and

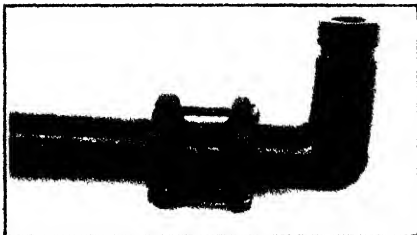


FIG. 64.

Method Used in Joining Havg Pipe.

Courtesy Havg Corporation

3 parts of ammonia. Reaction is carried on for 3 hours under reflux and the unreacted materials and water are removed by vacuum distillation. This product is suggested for use in varnishes or laminated materials. It may be hardened with hexamethylenetetramine under heat and pressure.

Novotny<sup>73</sup> carries out the condensation of xylenols and aldehydes in such a way that the water is removed substantially as fast as formed, preferably by distillation under atmospheric pressure. This method may be applied to the production of resins from xyleneol and furfural without the use of a catalyst. For example, 32 parts of commercial xyleneol and 21.2 parts of 37-40 per cent formaldehyde solution are placed in a digester equipped with a stirrer and a condenser for distillation. During a period of about 2 hours, 15-18 parts of distillate are collected. The temperature gradually rises during the distillation from 100°C. to about 140°C. at which temperature the product is found to be a hard, grindable resin. By stopping the distillation at a lower temperature soft resins are obtained. The reaction can be performed at a higher temperature (190°C.) if the condenser is equipped with a separator and siphon for returning the xylenols to the reaction mixture and discharging the water.<sup>74</sup> The apparatus in which this is done consists of a vessel in which the condensate separates into layers. The upper layer flows back into the reaction vessel, and the lower layer is drawn off.

<sup>66</sup> Carleton Ellis, U. S. P. 1,980,987, Nov. 20, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1935, 29, 524.

<sup>70</sup> A. A. Drummond and H. H. Morgan, British P. 345,276, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 324.

<sup>71</sup> D. G. Anderson and R. MacLaurin, British P. 183,629, 1921; *J.S.C.I.*, 1922, 41, 772A.

<sup>72</sup> G. E. Landt, U. S. P. 1,679,312, July 31, 1928, to Diamond State Fibre Co.; *Chem. Abs.*, 1928, 22, 3792.

<sup>73</sup> E. E. Novotny, U. S. P. 1,773,598, Aug. 19, 1930, to J. S. Stokes; *Brit. Chem. Abs.* B, 1931, 405

<sup>74</sup> E. E. Novotny, U. S. P. 1,793,715, Feb. 24, 1931, to J. S. Stokes; *Chem. Abs.*, 1931, 25, 2312.

Electrolytic oxidation of symmetrical xylenol in acid solution, followed by reduction with sulphur dioxide, yields m-xylohydroquinol and an insoluble resin.<sup>75</sup>

Resinous products proposed for use in the manufacture of varnishes are prepared by treating phenol alkyl ethers, e.g., m-cresol methyl ether, resorcinol diethyl ether or ar-tetrahydronaphthol alkyl ethers, with formaldehyde in the presence of acids. ar-Tetrahydronaphthol alkyl ethers are prepared by sulphonating tetrahydronaphthalene, fusing with alkali and treating the product with alkylating agents.<sup>76</sup> The methyl or ethyl ethers of symmetrical xylenol condense with formaldehyde in the presence of hydrochloric acid to form resins which are soluble in varnish oils (see Chapter 19), and which are also compatible with nitrocellulose.<sup>77</sup>

#### RESORCINOL AND OTHER POLYVALENT PHENOLS

Introducing additional hydroxyl groups in the phenol nucleus causes an increase in the rate of condensation with formaldehyde. The effect is even more marked than the reactivity-increase occasioned by the substitution of alkyl groups. Isolation of resorcinol alcohols as intermediate products in the condensation (see Chapter 14) is extremely difficult, since polymerization is so rapid.<sup>78</sup> At room temperature, resorcinol condenses with formaldehyde sufficiently rapidly that catalysts need not be added. Accordingly, the electrical properties of resorcinol resins are superior to those of resins which may contain traces of harmful constituents added as catalysts. Furthermore, resins from resorcinol or related compounds are characterized by higher tensile strength, less thermoplasticity and lower inflammability than the corresponding phenol-formaldehyde products.

Many years ago Fittig and Remsen prepared a pyrocatechol-formaldehyde resin, but they did not recognize the composition of their material, and mistook it for pure carbon.<sup>79</sup> Labbé<sup>80</sup> has treated pyrocatechol, resorcinol, pyrogallol, quinol and the like with a cold 40 per cent solution of formaldehyde in the presence of an acid to form materials which soon become gelatinous and after some hours are converted into homogeneous, elastic substances. Hard products are obtained by diluting the formaldehyde solution with half its volume of water. These resins are insoluble in water or organic solvents, are unattacked by alkalies and acids and are non-inflammable. The addition of acetone or glycerol to the formaldehyde results in the production of transparent stock. The physical properties of the products may be further modified by incorporating carbohydrates or cellulose. Amber-like substances such as are used in pipe stems have been produced by Peter<sup>81</sup> by heating 10 parts of resorcinol with from 7.5-10 parts of 40 per cent formaldehyde solution. Resins from resorcinol and paraformaldehyde are suitable for uniting layers of fabric or paper. The resin can be formed *in situ* and hardened under heat and pressure.<sup>82</sup> Sound records, made from resorcinol-aldehyde condensation product may be hardened by the use of ferric chloride.<sup>83</sup>

In 1930, wide publicity was given to resinous coatings on paper, used in the manufacture of flexible phonograph records and talking-picture discs. These are

<sup>75</sup> F. Fichter and M. Runderspacher, *Helv. Chim. Acta*, 1927, 10, 102, *Chem. Abs.*, 1927, 21, 1453.

<sup>76</sup> K. Marx, O. Siebert and H. Wesche, German P. 358,399 and 358,400, 1920, to Akt.-Ges. für Anilin-Fabr.; *J.S.C.I.*, 1922, 41, 948A.

<sup>77</sup> R. Hill, British P. 400,272, 1932, to Imperial Chem. Ind. Ltd.; *Brit. Chem. Abs. B*, 1934, 29. French P. 758,655, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 3256.

<sup>78</sup> T. Boehm and H. Porlanca, *Arch. Pharm.*, 1932, 270, 168; *Chem. Abs.*, 1932, 26, 2723.

<sup>79</sup> R. Fittig and I. Remsen, *Ann.*, 1871, 159, 129; 1873, 168, 96. P. Pascal, *Bull. soc. chim.*, 1925, 37, 1043; *Chem. Abs.*, 1925, 19, 3484.

<sup>80</sup> A. Labbé, French P. 468,379, 1913; *J.S.C.I.*, 1914, 33, 975.

<sup>81</sup> A. H. Peter, U. S. P. 1,147,264, July 20, 1916; *Chem. Abs.*, 1915, 9, 2433.

<sup>82</sup> British P. 346,411, 1928, to International General Elec. Co.; *Chem. Abs.*, 1933, 27, 283.

<sup>83</sup> S. Whyte, British P. 357,958, 1930, to Gramophone Co., Ltd.; *Chem. Abs.*, 1932, 26, 6166.

made<sup>85a</sup> by mixing 1000 cc. 40 per cent formaldehyde with 1000 g. resorcinol, and heating the solution slowly until the temperature rises to 70-75°C. The product is kept at this temperature, and stirred until the viscosity is suitable for coating paper. At this point it is rapidly cooled. Two hundred g. of rouge, ground with 600 g. of glycerol, is mixed with the resin, and the product is immediately applied to the paper.<sup>86</sup> Record impressions are embossed upon the coating by means of dies heated to 160°C., and no further hardening operation is required. In making records of this type, Billings and Hurst<sup>87a</sup> employed an emulsion of the resin instead of a solution. This is said to reduce the tendency of the sheets to curl, since the resin does not penetrate the fibers of the paper as much as when a solution is used. Beeswax and borax were employed as emulsifying agents in forming the colloidal dispersion of the resin.

McCoy<sup>88</sup> used pyrogallol and paraform in the presence of gum arabic to produce a red infusible resin. To harden fusible phenol-formaldehyde resins he<sup>89</sup> mixed them with pyrocatechol, tannin and paraformaldehyde (see Chapter 20). Polyvalent phenols are condensed with 40 per cent formaldehyde and sodium, calcium or zinc salts of hydrochloric, salicylic or benzenesulphonic acids are added to prevent shrinkage or development of brittleness.<sup>87</sup> Burmeister<sup>90</sup> prepared fairly rapid-curing compositions by condensing a solid formaldehyde derivative and resorcinol, with the addition of glycerol to control the speed of the condensation.<sup>88a</sup> For the preparation of lacquers which are to be baked after being applied, glycerol may be mixed with polyvalent phenol-formaldehyde resins, after the condensation has taken place.<sup>90</sup>

Resinous condensation products are obtained by Deutsche and Herrmann<sup>90</sup> by heating together polyvalent phenols and acetaldehyde, benzaldehyde or furfural, in the absence of catalysts. For use as a binder for fibrous materials Hawerlander<sup>91</sup> heats a mixture of 1 kg. of resorcinol with 1 l. of 40 per cent formaldehyde solution to 30°C. Three grams of sodium sulphate are then added and the mixture is heated to 75°C. and quickly cooled to 25°C. Sawdust, wood shavings, etc., after being moistened with a volatile liquid (gasoline) are treated with sufficient binding material to cover the surface of the fibrous particles and are then subjected to heat and pressure.<sup>92</sup> Grillet and Cottet<sup>93</sup> condense resorcinol with formaldehyde below 80°C., preferably in the absence of catalysts and in the presence of alcohol, glycerol or sugars. Water is eliminated from the products by distillation *in vacuo* below 50°C. Or the reaction mixture is poured into cold water or salt solution, while it is still viscous. The precipitate thus formed is

<sup>85a</sup> H. T. Beans, U. S. P. 1,915,282, June 27, 1933, to Durium Products Corp.; *Chem. Abs.*, 1933, 27, 4364. H. T. Beans, British P. 337,796, 1929, to Durium Products Corp.; *Chem. Abs.*, 1931, 25, 2255; *Brit. Chem. Abs.* B, 1931, 171. A. Hawerlander, U. S. P. 1,842,168, Jan. 19, 1932, to Durium Products Corp.

<sup>86</sup> The glycerol is used to impart flexibility. Instead of glycerol, a mixture of a raw fatty oil, a blown drying oil and a fatty acid of an oil has been suggested. H. P. Billings and D. A. Hurst, U. S. P. 1,999,717, Apr. 30, 1935, to Radio Corp. of America.

<sup>87a</sup> H. P. Billings and D. A. Hurst, U. S. P. 1,999,715, Apr. 30, 1935, to Radio Corp. of America.

<sup>88</sup> J. P. A. McCoy, U. S. P. 1,286,372, Dec. 3, 1918; *Chem. Abs.*, 1919, 13, 368.

<sup>89</sup> J. P. A. McCoy, U. S. P. 1,269,627, June 18, 1918; *Chem. Abs.*, 1918, 12, 1916.

<sup>90</sup> L. Helm, French P. 602,704, 1924; *Brit. Chem. Abs.* B, 1926, 889.

<sup>91</sup> H. Burmeister, British P. 275,678, 1926; *Brit. Chem. Abs.* B, 1927, 823.

<sup>88a</sup> It is said that good control of the speed of hardening is obtained by employing a resin from the condensation of resorcinol, cresol and formaldehyde in the presence of nitroaniline. The ratio of resorcinol to cresol is between 4:1 and 4:6 by weight. H. P. Billings and D. A. Hurst, U. S. P. 1,999,716, Apr. 30, 1935, to Radio Corp. of America.

<sup>92</sup> British P. 303,905, 1928, to International General Electric Co.; *Chem. Abs.*, 1929, 23, 4583.

<sup>93</sup> H. Deutsche and W. O. Herrmann, German P. 523,695, 1928, to Consortium für Elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 3856.

<sup>91a</sup> A. Hawerlander, British P. 342,278, 1929, to Halizite Corp.; *Chem. Abs.*, 1931, 25, 4894. U. S. P. 1,842,168, Jan. 19, 1932, to Durium Products Corp.; *Brit. Chem. Abs.* B, 1932, 1042.

<sup>92a</sup> A. Hawerlander, British P. 336,754, 1929, to Halizite Corp.; *Chem. Abs.*, 1931, 25, 1966.

<sup>93</sup> N. B. Grillet and E. C. Cottet, British P. 321,697, 1928, to Soc. des usines chim. Rhône-Poulenc; *Chem. Abs.*, 1930, 24, 2905. German P. 524,425, 1929; *Chem. Abs.*, 1931, 25, 3856. French P. 671,702, 1929; *Chem. Abs.*, 1930, 24, 2317.

washed and air-dried at a low temperature. Ward, Hereward and Ehrhardt<sup>94</sup> modify the process by replacing the resorcinol by a mixture of monovalent and polyvalent phenols. Similarly, Sprenger<sup>95</sup> prepared resins by mixing the condensation products of phenol and formaldehyde with those of resorcinol and formaldehyde, the proportion of resorcinol resin being, in some cases, about 70 per cent of the total. A filling or binding agent (sawdust) may be incorporated. Advantages to be gained by using mixtures of monovalent and polyvalent phenols are noteworthy. For instance, in dry reactions, resorcinol combines with formaldehyde so rapidly that some means must be applied for slowing up the rate. Resorcinol speeds up the phenol-formaldehyde reaction,<sup>96</sup> and reduces the danger of sticking or undercure.<sup>97</sup> Schuhmann and Hahn<sup>98</sup> condense resorcinol with only part of the equivalent amount of an aldehyde and the intermediate product so obtained is converted to an infusible insoluble product by treatment in a separate operation with additional aldehyde. The product can be mixed with fillers, coloring matter and natural or other synthetic resins.

Novotny<sup>99</sup> condenses 1 mol of resorcinol with 0.5 mol or less of paraformaldehyde in the absence of a catalyst at 100-150°C. and then cools the material below 100°C. before the reaction product becomes infusible. Additional paraformaldehyde may then be admixed as hardening agent. The resin may be used in varnishes and coating compositions or in other ways. If the resin is heated, hard but still-fusible resinous material results.<sup>100</sup> Since the condensation of a small amount of resorcinol seems to aid in accomplishing a rapid condensation of phenol with formaldehyde, Novotny<sup>101</sup> makes use of resorcinol to assist the hardening of phenol-formaldehyde resins. For example, to obtain a potentially-reactive soluble product of rapid reactivity 15 parts resorcinol, 45 parts phenol and 31 parts paraformaldehyde are employed. These are heated to 100°C. until the mixture is clear and the desired viscosity has been obtained. Alcohol may be added to stop the reaction, or if a solid dry resin is desired the material can be placed in pans and rapidly cooled. Moss<sup>102</sup> condenses resorcinol or its isomers with acetone (see also Chapter 25), in the presence, preferably, of concentrated hydrochloric, sulphuric or phosphoric acid. A yellow oil, which gradually is converted into a yellow-pink solid, is the product. The reaction requires 24 hours at room temperature or 1 hour at 60-70°C. The resin is said to be compatible with cellulose acetate, both in solution and in plastic compositions.

Besides the polyvalent phenols which have been discussed above, many other phenolic bodies have been used in the preparation of resins. Some of these yield oil-soluble compositions, and will be described in Chapter 19.

Adhesive compositions for reinforced glass may contain cellulose acetate and a resin (e.g., from hydroxybenzyl alcohol), modified by glycerol.<sup>103</sup> The dihydroxybenzophenones condense with aldehydes in the presence of acid catalysts (including zinc and aluminum chlorides), and the resins thus obtained are suggested for

<sup>94</sup> W. W. Ward, P. O. Hereward and E. F. Ehrhardt, British P. 325,861, 1928, to Soc. des usines chim. Rhône-Poulenc; *Chem. Abs.*, 1930, 24, 4175. German P. 531,949, 1929; *Chem. Abs.*, 1932, 26, 611. French P. 679,537, 1929; *Chem. Abs.*, 1930, 24, 3915.

<sup>95</sup> R. Sprenger, German P. 536,553, 1928, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1932, 26, 1144. German P. 538,553, 1929; *Chem. Abs.*, 1932, 26, 3126. French P. 667,207, 1929; *Chem. Abs.*, 1930, 24, 1236. British P. 350,934, 1930, to International General Electric Co.; *Brit. Chem. Abs. B*, 1931, 853.

<sup>96</sup> British P. 221,475, 1923, to Riblu-Record Akt.-Ges. Polyvalent phenols also catalyze the urea-formaldehyde reaction. See Chapter 30.

<sup>97</sup> J. J. Kessler, U. S. P. 1,889,751, Dec. 6, 1933, to Apple Electrical Mfg. Co.; *Chem. Abs.*, 1933, 27, 1724.

<sup>98</sup> H. Schuhmann and E. Hahn, German P. 540,112, 1929, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1932, 26, 3945. French P. 691,464, 1930; *Chem. Abs.*, 1931, 25, 1400.

<sup>99</sup> E. E. Novotny, U. S. P. 1,767,696, June 24, 1930, to J. S. Stokes; *Chem. Abs.*, 1930, 24, 4409.

<sup>100</sup> E. E. Novotny, U. S. P. 1,849,109, Mar. 15, 1932, to J. S. Stokes; *Chem. Abs.*, 1932, 26, 2879.

<sup>101</sup> E. E. Novotny, U. S. P. 1,802,390, Apr. 28, 1931, to J. S. Stokes; *Chem. Abs.*, 1932, 26, 437.

<sup>102</sup> W. H. Moss, Canadian P. 319,549, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 2334. British P. 368,801, 1930, to Brit. Celanese, Ltd.; *Chem. Abs.*, 1933, 27, 2319.

<sup>103</sup> British P. 365,094, 1930, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1932, 357.

use with cellulose esters<sup>104</sup> in the preparation of a transparent adhesive employed in the manufacture of laminated glass. A number of modifiers are included in the adhesive product, which may contain simultaneously the following: cellulose nitrate, camphor, dibutyl phthalate, synthetic resin, benzene, alcohol, butyl alcohol, butyl acetate and ethyl acetate. Dihydroxybenzophenone is prepared<sup>105</sup> by condensing phenol with carbon dioxide at 70 atmospheres and 105-110°. Corresponding compounds are obtained from the cresols, but resorcinol and  $\beta$ -naphthol are too reactive, and resinification occurs before the substituted benzophenone can be isolated. At higher pressures phenol reacts with carbon dioxide to yield salicylic acid.

#### SALICYLIC ACID AND OTHER PHENOLIC SUBSTANCES

By condensing aromatic hydroxycarboxylic acids with aldehydes a series of resins soluble in mild alkalis has been obtained<sup>106</sup> (see also Chapter 20). Salicylic acid, for example, may be heated with 30 per cent aqueous formaldehyde for 20 hours to give a white precipitate. This is separated, freed from excess water and further heated until a sample sets to a clear glass-like substance. The duration of treatment may be shortened by the addition of hydrochloric acid. The hard resin obtained is soluble in alcohol, acetone or weak alkalis. It is suggested for leather finishing and for treating felts in the manufacture of hats. Similar resins are obtained from hexamethylenetetramine and mixtures of *o*- and *p*-hydroxybenzoic acids, from 1,3,4-hydroxytoluic acid and paraformaldehyde in the presence of ammonium acetate and from salicylic acid and benzaldehyde in the presence of ammonia. These products are yellow to yellowish red in color, and are soluble in weak alkalis. Two mols of salicylic acid may be condensed with 1 mol of formaldehyde to give a dihydroxydiphenylmethane dicarboxylic acid. The latter product is then caused to react with a monobasic acid such as rosin or tung oil acid and glycerol to yield a product to be incorporated in cellulose ester lacquers.<sup>107</sup>

Conditions necessary for the preparation of resins from various aromatic acids are as follows: *m*-hydroxytoluic acid with formaldehyde in alkaline solution at 30°C.; *o*-methoxybenzoic acid, formaldehyde and concentrated sulphuric acid at 100°C.; *o*-ethoxybenzoic acid and formaldehyde at 140-150°C. under pressure; 2-ethoxynaphthalene-3-carboxylic acid at 100°C. with paraformaldehyde in the presence of acetic and concentrated hydrochloric acids; a mixture of *o*-, *m*- and *p*-hydroxytoluic (cresotinic) acids with acetaldehyde at 130-140°C. under pressure in the presence of zinc chloride.<sup>108</sup> Esters of these aromatic hydroxycarboxylic acids may be used<sup>109</sup> to produce resins which are almost insoluble in alcohol, benzene or dilute alkali, but soluble in ether, amyl acetate or ethyl acetate. They can be used to prepare lacquers which are unaffected by light. Concentrated sulphuric acid, concentrated hydrochloric acid, zinc chloride or glacial acetic acid are used to catalyze the condensation of ethyl or phenyl salicylate with formaldehyde at 100°C. The methyl ester of hydroxytoluic acid (cresotinic acid) reacts with paraformaldehyde at 100°C. in the presence of zinc chloride and glacial acetic acid, and the ethyl ester of *p*-hydroxybenzoic acid combines with methylal when these sub-

<sup>104</sup> W. H. Moss, U. S. P. 1,954,826, April 17, 1934, to Celanese Corp. of America; *Chem. Abs.*, 1934, 28, 3922. Canadian P. 319,550, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 2324. W. H. Moss, Canadian P. 325,615, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 5777. British P. 417,519, 1934, to British Celanese, Ltd.; *Brit. Chem. Abs. B.*, 1934, 1110; *Chem. Abs.*, 1935, 29, 1176.

<sup>105</sup> G. T. Morgan and D. D. Pratt, British P. 353,464, 1930; *Chem. Abs.*, 1932, 26, 5308.

<sup>106</sup> German P. 339,495, 1919, to Meister, Lucius & Brünig; *J.S.C.I.*, 1922, 41, 639A.

<sup>107</sup> O. A. Cherry, U. S. P. 1,982,788, Dec. 4, 1934, to Economy Fuse & Manufacturing Co.; *Chem. Abs.*, 1935, 29, 523.

<sup>108</sup> German P. 357,757, 357,758, and 358,401, 1920, to Farb. vorm. Meister, Lucius & Brünig, *J.S.C.I.*, 1922, 41, 948A.

<sup>109</sup> A. Voss, German. P. 364,044, 1920, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 614A.

stances are heated together under pressure at 120°C. Pink<sup>110</sup> prepared a reaction product of salicylic acid with a molecular proportion of hexamethylenetetramine in alcoholic solution. The solvent is removed and a viscous syrup is formed which gives a reddish precipitate with ferric chloride. A resin intended for dental use is made by Andresen<sup>111</sup> by condensing eugenol with formaldehyde. The reacting materials may be mixed with burnt alum, and the pasty condensation product mixed with zinc oxide.

The hydroxybenzoic acids have a tendency to form resins as a result of oxidation, reduction and dehydration reactions. Von den Velden<sup>112</sup> observed that the reduction of 2- and 4-hydroxybenzoic acids with sodium amalgam in acid solution yielded resinous matter, and Perkin,<sup>113</sup> oxidizing 3-hydroxybenzoic acid with potassium persulphate in an aqueous sulphuric acid solution at 30°C. for 12 hours, obtained some colored resinous bodies. Salicylic acid upon dehydration gives complex anhydride substances that do not melt when heated though by treatment with alkali may be hydrolyzed back to the parent substance. Phosgene acting on a pyridine solution of salicylic acid gave disalicylic acid anhydride and amorphous dehydration products.<sup>114</sup> A complex mercury anhydride  $-(C_7H_3O_2Hg)_n-$  was obtained by heating at 100°C. an aqueous solution of salicylic acid with mercuric oxide.<sup>115</sup>

Aryloxyaliphatic acids are heated with formaldehyde or a substance which yields formaldehyde to produce hard resins which are almost colorless and transparent, easily soluble in alcohol, acetone and other organic solvents and in mild alkalies.<sup>116</sup> For example, phenoxyacetic acid when boiled under reflux with 40 per cent formaldehyde solution in the presence of hydrochloric acid yields a colorless oil lighter than water. This oil, when washed several times with water, can then be heated in an open vessel at 120-130°C. until a test portion solidifies on cooling. Products of analogous properties can be obtained from cresoxyacetic acid, xylyloxyacetic acid,  $\alpha$ - or  $\beta$ -naphthoxyacetic acid, or from the corresponding propionic and butyric acids. Pyrocatecholmonoacetic acid also gives a similar product when treated with formaldehyde. The use of a quantity of aldehyde less than equivalent to the aryloxyaliphatic acid renders the process more easily controllable. At increased pressures and temperatures the condensation proceeds much more rapidly and the use of catalysts may be omitted. Binding agents for anti-halation materials for use on photographic plates are alkali-soluble resins derived from salicylic acid and paraldehyde, from phenoxyacetic acid and formaldehyde or from o-methoxybenzoic acid and formaldehyde.<sup>117</sup> Aliphatic or aromatic aldehyde- or keto-carboxylic acids, which contain the carboxyl group either in the nucleus or in the side chain, can be condensed with phenols or naphthols by the use of catalysts, such as hydrogen chloride.<sup>118</sup> For example, m-aldehyde-phenoxyacetic acid is melted with phenol and treated at 40-50°C. with concentrated hydrochloric acid to obtain a hard resin. By the action of chloroacetic acid on 2-aldehyde-4-methyl-phenol the compound 2-aldehyde-4-methyl-phenoxyacetic acid is obtained, which, condensed with  $\alpha$ -naphthol, also yields a resin.

Benzophenone-2,4-dicarboxylic acid can be condensed with m-cresol. The

<sup>110</sup> L. Pink, U. S. P. 1,825,636, Sept. 29, 1931; *Chem. Abs.*, 1932, 26, 155.

<sup>111</sup> V. J. Andresen, *Brit. Pat.* 110,154, 1917; *Chem. Abs.*, 1918, 12, 410.

<sup>112</sup> A. von den Velden, *J. prakt. Chem.*, 1877, 15 (2), 164; *J.C.S.*, 1877, 32, 337.

<sup>113</sup> A. G. Perkin, *J.C.S.*, 1905, 87, 1425.

<sup>114</sup> A. Einhorn and H. Pfeiffer, *Ber.*, 1901, 34, 2951; *J.C.S.*, 1901, 80 (1), 712.

<sup>115</sup> H. Jajoux and A. Grandval, *Comp. rend.*, 1893, 117, 45; *J.C.S.*, 1893, 64 (1), 642. O. Dimroth, *Ber.*, 1902, 35, 2872; *J.C.S.*, 1902, 82 (1), 656. G. Buroni, *Gazz.*, 1902, 32 (2), 307; *J.C.S.*, 1903, 84 (1), 392.

<sup>116</sup> German P. 364,040, 1919, 371,147, 1920 and 371,149, 1920, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 613A, 1140A.

<sup>117</sup> British P. 399,713, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 1085.

<sup>118</sup> German P. 362,382, 1920, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 613A.

resin from glyoxylic acid and phenol has an especially bright yellow color in caustic soda solution.

o-Benzoylbenzoic acid condenses<sup>119</sup> with phenols (xlenols, cresols, naphthols) in the presence of concentrated sulphuric acid to form amber-like brittle resins. The temperature is kept lower than that at which esterification or anthraquinone formation takes place. Resins made in this way readily undergo further condensation with formaldehyde, furfural or acetaldehyde, especially in the presence of ammonia, to yield fusible soluble products which, when mixed with cellulose esters, are capable of forming transparent films. Typical keto-aromatic acids which may replace o-benzoylbenzoic are  $\alpha$ -hydroxy-o-naphthoylbenzoic or 2',5'-dichloro-2-benzoylbenzoic acids. Resinous products are obtained<sup>120</sup> either by (1) treating mixtures of phenols and aromatic carboxylic acids with aldehydes, or substances capable of yielding aldehydes, preferably in the presence of alkalis, or by (2) reacting phenols and carboxylic acids separately with aldehydes, and subsequently causing the products to interact, or, by (3) treating mixtures of phenol-aldehyde condensation products and carboxylic acids, or of carboxylic acid-aldehyde condensation products and phenol with aldehydes. Whichever method is adopted, the products are separated from solution, and heated to temperatures above 100°C. to obtain resins soluble in dilute alkalis.



FIG. 65.  
Digestion Tank of Haveg Reinforced  
with Steel Ribs.

*Courtesy Haveg Corp.*

Glycol-monoaryl ethers can be heated with formaldehyde in the presence of an acid to produce resin-like substances<sup>121</sup>. Thus, for example, ethyleneglycol-monophenyl ether,  $C_6H_5-O-CH_2-CH_2OH$ , is heated with formaldehyde in the presence of 3.5 per cent hydrochloric acid, with the addition of phenols. The ethers of the phenols may be used in place of the phenols. From formaldehyde and glycol-monophenyl ether and the hydroxyethyl ethers of the cresols or the naphthols, viscous, almost colorless oils, insoluble in alkali, soluble in acetone, benzene, amyl acetate and cyclohexanone are first obtained and are of use in the rubber industry. On long standing or on heating to above 80°C. they form extremely elastic, gummy substances, which can be kneaded. They do not melt, and are insoluble in all the usual solvents. They can be used to increase the elasticity of other synthetic resins by combining their preparation with that of the synthetic resin involved and giving the mixture a final heating to cause the intermediate glycol compound to assume the plastic form. Formaldehyde may be condensed in large excess with a phenol having a long saturated hydrocarbon side-chain such as thymol, p-ter-butylphenol, o- and p-cyclohexylphenol,

<sup>119</sup> H. A. Bruson, U. S. P. 1,934,032, Nov. 7, 1933, to Resinous Products & Chemical Co.; *Chem. Abs.*, 1934, 28, 663.

<sup>120</sup> German P. 386,733, 1920, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1924, 43, 604B.

<sup>121</sup> German P. 364,042, 1920, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 564A.



o-phenylphenol and  $\beta$ ,  $\beta'$ -bis(4-hydroxy-3-methylphenyl) propane. The condensation takes place in contact with an energetic base.<sup>122</sup>

Harvey<sup>123</sup> condenses cashew-shell oil (a phenolic material) with aldehydes, in the presence or absence of catalysts, to produce synthetic resins that may be subsequently hardened. For details, see Chapter 61. Aryl esters of aliphatic acids are condensed by Seebach with compounds containing active methylene groups, to obtain resinous products.<sup>124</sup> Thus, hexamethylenetetramine is condensed with diphenylcarbonate,  $(C_6H_5)_2CO_2$ , to give a solid product. The reaction can be performed by simply pressing the two powdered substances together, with the application of heat. The product is said to be fully hardened within a few minutes. In fact, careful control of the relative amounts of reactants is necessary, lest the reaction become too violent.

A resinous composition for molding is prepared by Ellis<sup>125</sup> from cyclohexanol and formaldehyde. Ten parts of cyclohexanol, for example, are heated with 3 parts of paraformaldehyde and 5 parts of 50 per cent aqueous potassium hydroxide solution for 3 hours. The resinous material is dissolved in benzene and, on evaporating, a dark-brown clear transparent fusible resin is obtained. To this can be added 5-10 per cent of hexamethylenetetramine, and fillers, and the product can be molded under heat and pressure or it can be molded cold and baked carefully to bring about the hardening reaction. Moss<sup>126</sup> prepared resins compatible with cellulose acetate from a diphenylnaphthene and formaldehyde. For example, 264 parts of diphenylol cyclohexane, resulting from the condensation of phenol with cyclohexanone,<sup>127</sup> 75 parts of 40 per cent formaldehyde solution and 66 parts of phosphoric acid are heated under reflux until a resin is obtained which solidifies at about 50°C. It is purified by washing with water. Fusible resins can be treated for the removal of free phenol or formaldehyde by reaction with cyclohexanone.<sup>128</sup> Condensation products made by interaction of a phenol ( $\beta$ -naphthol, 4,4'-dihydroxy- $\beta$ , $\beta'$ -diphenylpropane) with formaldehyde and an alkyl- or cycloalkyl-amine (piperidine, piperazine) have been proposed as anti-agers for rubber.<sup>129</sup>

The condensation of diarylacetals with formaldehyde to yield resins has also been accomplished.<sup>130</sup> When 2 mols of acetal are condensed with 1 mol or less of formaldehyde, viscous oils or soft resins which liquefy without decomposition at high temperatures and are soluble in organic solvents are produced. Larger proportions of formaldehyde give viscous, insoluble, less fusible resins.

Dreyfus and Schneider<sup>131</sup> have utilized the thiophenols (see Chapter 59) in place of phenols for preparing resins which can be incorporated in lacquers containing cellulose esters. Such compounds as the thiocresols,<sup>132</sup> thioxylanols, benzyl mercaptan or di-thiophenylol propane condense with formaldehyde or acetaldehyde. Acid or alkaline catalysts may be used, but are not necessary. The resin and cellulose derivative are dissolved in a mutual solvent, and plasticizers

<sup>122</sup> H. Hönel, J. Ehrenfeld and O. Reichhold, British P. 417,122, Sept. 24, 1934, to Beck, Koller & Co.; *Chem. Abs.*, 1935, 29, 1180.

<sup>123</sup> M. T. Harvey, British P. 283,803, 1926; *Brit. Chem. Abs. B*, 1928, 237.

<sup>124</sup> F. Seebach, German P. 542,786, 1929, to Bakelite G.m.b.H.; *Chem. Abs.*, 1932, 26, 3393. U. S. P. 1,933,124, Oct. 31, 1933, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 664.

<sup>125</sup> Carleton Ellis, U. S. P. 1,557,521, Oct. 13, 1925; *Chem. Abs.*, 1926, 20, 301.

<sup>126</sup> W. H. Moss, U. S. P. 1,873,849, Aug. 23, 1932, to Celanese Corp. of America. Canadian P. 319,730, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 6166.

<sup>127</sup> See Chapters 18 and 25.

<sup>128</sup> K. H. Schuch, German P. 567,072, 1930, to Aug. Nowack A.-G.; *Chem. Abs.*, 1933, 27, 1464.

<sup>129</sup> H. M. Bunbury, J. S. H. Davis and W. J. S. Naunton, British P. 375,360, 1931, to Imperial Chem. Ind. Ltd.; *Brit. Chem. Abs. B*, 1932, 928.

<sup>130</sup> German P. 397,315, 1922, to Farb- u. v. m. Meister, Lucius & Brüning; *J.S.C.I.*, 1924, 43, 879.

<sup>131</sup> C. Dreyfus and G. Schneider, U. S. P. 1,860,262, May 29, 1934, to Celanese Corp. of America; *Chem. Abs.*, 1934, 28, 4616. Canadian P. 325,064, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 5440. British P. 367,759, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1933, 27, 2053.

<sup>132</sup> Aldehydes condense more rapidly with thiocresols than with cresols. G. L. Stadnikov, N. M. Gavrilov and V. E. Rakovskii, *J. Chem. Ind. (Moscow)*, 1925, 2, 315.

(triacetin, diethyl tartrate, dibutyl tartrate) are added. It is also possible to prepare a sulphur-containing resin of the phenol-aldehyde type by condensing thioformaldehyde or thioacetaldehyde with phenol. Still another alternative is to condense phenol and formaldehyde in the presence of ammonium sulphide. The reaction requires 6 hours at 180°C. under increased pressure.<sup>133</sup> Other sulphur resins are discussed in Chapter 59.

### CHLORINATED PHENOLS

Resins made by condensing chlorinated phenol<sup>134</sup> with formaldehyde<sup>135</sup> are characterized by being chemically inert and practically non-inflammable. Aylsworth (see also Chapter 20) prepared chlorinated phenol-aldehyde resins,<sup>136</sup> and used them for incorporation with phenol-formaldehyde products. Steinmetz<sup>137</sup> specified the following procedure: about 136 parts of monochlorophenol are mixed with 75-100 parts of 40 per cent formaldehyde solution, and the mixture is heated under reflux with 5-10 per cent hexamethylenetetramine. A soluble fusible resin is formed, which can be hardened by the addition of sufficient quantities of hexamethylenetetramine.

Brunner<sup>138</sup> treats an aqueous solution of formaldehyde and phenol at 40-45°C. with concentrated hydrochloric acid to obtain a viscous resin, or at 5-10°C. to obtain 6,8-bischloromethylbenz-1,3-dioxan, melting at 117°C. p-Cresol at 20°C. gives 3,5-bischloromethyl-p-cresol, melting at 86°C. while technical cresols at 40°C. give a resin. Faster reactions at higher temperatures give resinous products. The products can be further condensed with phenols, hydrogen chloride being eliminated. The crystalline compounds are intermediates for the preparation of dyestuffs, synthetic resins and tanning materials.

A mixture of benzoyl cyanide and resorcinol dissolved in dry ether containing a small quantity of zinc chloride, saturated in the cold with hydrogen chloride, quickly deposits a reddish-brown resin.<sup>139</sup>

Datta and Prosad<sup>140</sup> dissolved the three isomeric hydroxybenzoic acids in aqueous ammonia and treated with iodine. The expected iodo-acid was crystallized from acetic acid but complex pink-colored material was also obtained insoluble in boiling solvents. p-Hydroxybenzoic acid gave a complex anhydride when heated with phosphorus oxychloride in ether solution.<sup>141</sup> This has been extended to cover mixtures of hydroxybenzoic acids or their homologues by treatment with acetyl chloride or acetic anhydride, to form resins soluble in acetone, aromatic hydrocarbons and linseed oil. Such solutions applied to wood yield hard glossy films

<sup>133</sup> G. Brunn, Austrian P. 100,564, 1921; *Brit. Chem. Abs.* B, 1926, 890.

<sup>134</sup> Chlorinated toluene reacts with phenol to produce resins. These are described in Chapter 56.

<sup>135</sup> A large number of crystalline substances of the general formula  $\text{HOR}_1\text{CHXR}_2\text{OH}$ , where  $\text{R}_1$  and  $\text{R}_2$  are halogenated benzene residues, and X is hydrogen or an alkyl or aryl group, have been prepared by reacting halogenated phenols with formaldehyde. Such compounds are useful as moth-repellants. M. Weiler, B. Wenk and H. Stötter, U. S. P. 1,707,181, March 26, 1929; *Chem. Abs.*, 1929, 23, 2257. M. Weiler, B. Wenk and H. Stötter, Canadian P. 284,773, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 942. British P. 330,893 and 330,894, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 896. British P. 333,561, 1929; *Brit. Chem. Abs.* B, 1930, 1017. British P. 316,900, 1928; *Brit. Chem. Abs.* B, 1929, 888. British P. 335,547, 1929; *Brit. Chem. Abs.* B, 1931, 13. French P. 651,646, 1928, and addn. 39,685, 1930; *Chem. Abs.*, 1929, 23, 3316; 1932, 26, 4827. British P. 383,493, 1932; *Brit. Chem. Abs.* B, 1933, 140. M. Weiler, K. Beires, B. Wenk and H. Stötter, U. S. P. 1,906,890, May 2, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3624.

<sup>136</sup> J. W. Aylsworth, U. S. P. 1,046,137, Dec. 8, 1912, Reissue 13,531, Feb. 11, 1913; *Chem. Abs.*, 1915, 9, 712.

<sup>137</sup> C. P. Steinmetz, U. S. P. 1,215,072, Feb. 6, 1917; *Chem. Abs.*, 1917, 11, 1048. Chlorophenol-formaldehyde resins here found use as coatings for fabrics. See Chapter 21.

<sup>138</sup> A. Brunner, German P. 550,326, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4065. British P. 347,887, 1930; *Brit. Chem. Abs.* B, 1931, 711. A. Brunner, U. S. P. 1,807,729, June 2, 1931, to General Aniline Works; *Chem. Abs.*, 1931, 25, 4268.

<sup>139</sup> W. Borsche and C. Walter, *Ber.*, 1926, 59, 468.

<sup>140</sup> R. L. Datta and N. Prosad, *J.A.C.S.*, 1917, 39, 447.

<sup>141</sup> E. Fischer and K. Freudenberg, *Ann.*, 1910, 372, 45; *Chem. Abs.*, 1910, 4, 2123.

reported to be resistant to chemical reagents, oxidation, moisture and to light<sup>142</sup> Silver salts of certain halogenated phenols have the property of splitting out silver halide to form amorphous compounds for which cryoscopic measurements indicated molecular weights from 2000-5000. Thus, the silver salt of symmetrical triiodophenol, in dry benzene with a trace of iodine, gave amorphous substances of the composition  $(C_6H_2I_3O)_n$ . Similar polymers can be made from the potassium or sodium salts of symmetrically trihalogenated phenols.<sup>143</sup>

<sup>142</sup> German P. 344,034, 1920, to Farb- u. v. Meister, Lucius & Brüning; *J S C I*, 1922, 41, 301A

<sup>143</sup> W. H. Hunter and G. H. Woollett, *J A C S*, 1921, 43, 135

## Chapter 18

### Phenol-Aldehyde Resins

#### VI. Employment of Other Aldehydes

In the manufacture of phenol-aldehyde resins other aldehydes may be used in place of formaldehyde and its polymers. For instance, acetaldehyde, butyraldehyde, benzaldehyde, furfural,<sup>1</sup> carbohydrates<sup>2</sup> (such as sucrose), glycerol (which is readily dehydrated to acrolein), aldehyde derivatives (methylals) and some unsaturated hydrocarbons, e.g., acetylene (which in many of its reactions behaves as if it were the anhydride of acetaldehyde<sup>3</sup>) have been suggested. In addition, ketones, for example, acetone, may be condensed with phenols to yield either resins or compounds which give resinous bodies on treatment with aldehydes. A discussion of the latter types of substances is also included in this chapter. The employment of all these materials in place of formaldehyde is of course contingent on some advantage to be gained thereby, such as a cheaper product, or one with more desirable characteristics.

##### ACETALDEHYDE

Phenol combines with acetaldehyde to form crystalline derivatives, though the reactions may be directed in such a manner that the major portion of the yield is resinous.<sup>4</sup> In general, synthesis of soluble fusible materials is effected and there is little danger of an infusible product being formed. In order to obtain infusible masses, such as are desired in the manufacture of cast articles, moldings and varnishes, more active methylene-containing agents are generally used, e.g., formaldehyde, paraformaldehyde and hexamethylenetetramine.

A water-soluble resin can be prepared by adding 44 parts of acetaldehyde to a cooled solution of 216 parts of crude cresol in 100 parts of sulphuric acid (sp.gr. 1.83) and 1000 parts of alcohol and heating under reflux.<sup>5</sup> Afterwards the alcohol is distilled off with steam and the residue poured into cold water, from which crude dihydroxyditolylethane separates as a hard resin. This is broken up and added to 500 parts of sodium sulphite dissolved in water and 200 parts of 30 per cent formaldehyde are added. The mixture is warmed to dissolve the material and is then heated for 5-6 hours at 95-100°C. The solution is neutralized, filtered to free from precipitated impurities, and evaporated to dryness.<sup>6</sup>

In another procedure phenol is condensed with acetaldehyde, paraldehyde, metaldehyde or tetraldehyde, in the presence of acids, bases, neutral, basic or acid

<sup>1</sup> See Chapter 24 for phenol-furfural resins.

<sup>2</sup> See Chapter 36 for phenol-carbohydrate resins.

<sup>3</sup> J. A. Nieuwland and S. A. Flood, *J.A.C.S.*, 1928, 50, 2566. W. Heckel and P. Nashan (U. S. P. 1,943,385, Jan. 16, 1934, to Gutehoffnungshütte Oberhausen A.-G.; *Chem. Abs.*, 1934, 28, 2018) have suggested a catalytic treatment of acetylene as a means of procuring acetaldehyde.

<sup>4</sup> Mention has already been made (Chapters 13 and 16) of the observations of A. Baeyer, *Ber.*, 1872, 5, 1095; A. Claus and E. Tramer, *Ber.*, 1886, 19, 3004; J. Abel, *Ber.*, 1892, 25, 3477 and A. Smith, U. S. P. 643,012, Feb. 6, 1900 on the reaction of acetaldehyde with phenol.

<sup>5</sup> Swiss P. 71,652, 1916, to Badische Anilin- & Soda Fabrik.

<sup>6</sup> Sulphite waste-liquor has been suggested as a source of acetaldehyde. See O. W. Knight, U. S. P. 1,143,714, June 22, 1915. See Chapter 36.

salts, to obtain a fusible resin. The latter is soluble in benzene and alcohol and can be further treated with formaldehyde to give an insoluble infusible resin.<sup>7</sup> For instance, 100 g. of phenol or cresol<sup>8</sup> are used with 2 cc. of concentrated hydrochloric acid and 46 g. of acetaldehyde. Kendall<sup>9</sup> obtained a fusible resin capable of being hardened with an active methylene-producing agent, by reacting 100 parts of phenol with 25 parts of acetaldehyde and approximately 2 parts of hydrochloric acid or a small proportion of sulphuric acid.

Steindorff and Balle<sup>10</sup> suggested that reaction between acetaldehyde and phenols (or cresols) be carried out in solvents such as carbon tetrachloride or trichloroethylene. Condensing agents, e.g., hydrochloric acid, sulphuric acid and thionyl chloride, were employed. The products were yellow resins soluble in the usual organic solvents, in linseed oil and in solutions of caustic alkali, and insoluble in aqueous alkali bicarbonate. As an example, technically distilled cresol is dissolved in an equal weight of carbon tetrachloride, concentrated hydrochloric acid is added and the mixture stirred with paraldehyde at 25-30°C. for 16 hours. It is then neutralized and steam-distilled to recover the solvent and any unreacted cresol and the resin is thoroughly washed with warm water.

A condensation product from acetaldehyde and phenol or cresol was employed by Novotny<sup>11</sup> for impregnating fibrous blanks which are to be used for making such articles as phonograph records, panels and gears. One hundred parts of phenol and 75 parts of acetaldehyde are brought into reaction by means of a catalyst (hydrochloric or sulphuric acid). The acid is removed by blowing with steam or by neutralizing with ammonia. The resin so prepared does not harden readily on heating but retains its thermoplastic properties for a long period. Protracted baking in an oven will, however, bring about hardening to an infusible form. Hence it may be cold molded. The addition of 2 per cent of nigrosine black or zinc chloride as a final catalyst assists in the hardening. An intermediate product may be made from 100 parts of phenol and 35 parts of acetaldehyde in the presence of an acid and adding an acetaldehyde compound of sodium bisulphite as a hardening agent. Impregnation of paper, cardboard or other supports is effected by using a solution of the condensation product in a mixture of benzol and alcohol. A 5 per cent solution was recommended by Novotny.

A resinous substance which remains soluble and fusible on heating was obtained by Potter and Fleet<sup>12</sup> by condensing phenol or its homologues with acetaldehyde or its polymers. The proportions used were 100 parts by volume of phenol, 75 parts of paraldehyde and 5 parts of concentrated sulphuric acid. Similarly 100 parts of phenol, 45 parts of paraldehyde, 45 parts of 40 per cent formaldehyde and 5 parts of ammonium hydroxide (sp.gr. 0.88) may be used. More formaldehyde (or one of its polymers) can be added at some stage of the process to reduce the solubility and fusibility of the resulting material.

A readily fusible resin was made from phenol and acetaldehyde by Ellis,<sup>13</sup> employing an excess of phenol, and an acid catalyst, e.g., sulphuric acid. The product, after hardening treatment with furfural (aided by a mild alkaline catalyst such as sodium carbonate), can be incorporated with hexamethylenetetramine<sup>14</sup> and the resulting mixture used for molding. Clear, readily soluble substances

<sup>7</sup> Swiss P. 85,872, 1920, to Bakelite G.m.b.H.

<sup>8</sup> Swiss P. 87,893, 1921, to Bakelite G.m.b.H.

<sup>9</sup> D. S. Kendall, British P. 189,164, 1922, to Condensite Co.; *J.S.C.I.*, 1922, 41, 558A. Canadian P. 232,251, 1922; *Chem. Abs.*, 1923, 17, 2941.

<sup>10</sup> A. Steindorff and G. Balle, German P. 365,286, 1920, to Farb- u. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 614A.

<sup>11</sup> E. E. Novotny, U. S. P. 1,370,666, Mar. 8, 1921; *Chem. Abs.*, 1921, 15, 1975. See also British P. 178,828, 1920.

<sup>12</sup> H. Potter and W. Fleet, British P. 169,347, 1921, to Damard Lacquer Co., Ltd.; *J.S.C.I.*, 1921, 40, 780A.

<sup>13</sup> Carleton Ellis, U. S. P. 1,592,296, July 13, 1926; *Chem. Abs.*, 1926, 20, 3242

<sup>14</sup> Carleton Ellis, U. S. P. 1,592,773, July 13, 1926; *Chem. Abs.*, 1926, 20, 3242.

result from the action of gaseous aldehydes (diluted with inert gases, e.g., nitrogen or carbon dioxide) upon phenols or solutions containing them.<sup>15</sup> For example, a mixture of acetaldehyde vapor and carbon dioxide is passed at 50°C. for about 5 hours through phenol containing a little dilute hydrochloric acid.

Paraldehyde may be substituted for acetaldehyde. Thus, Ellis<sup>16</sup> obtained a hard brittle resin by slowly adding 4 lb. of paraldehyde to 8 lb. of phenol, containing 1 fluid ounce of concentrated hydrochloric acid. The mixture became hot and was allowed to stand over night, after which it was heated to 150°C. under reflux for 1 hour. The resulting resin, with 10 per cent of hexamethylenetetramine, dissolved in an equal weight of denatured alcohol, was incorporated with the same weight of wood flour. The mix was dried in a vacuum oven. In the molding press, discs of the dried material cured readily in 2 minutes at 160°C. and 1000 lb. pressure. Aluminum palmitate or some other water-insoluble soap, blended with the resin in powder form, was effective in preventing sticking during molding.

A soluble fusible condensation product was made by Baekeland and Gotthelf<sup>17</sup> by heating 1000 g. of phenol with 550 g. of paraldehyde and 50 cc of concentrated hydrochloric acid. The water separated into a distinct layer and was removed. Addition of an agent with an active methylene group transformed the resin into a material capable of further hardening. Crystalline dihydroxydiphenylethane, prepared from acetaldehyde and phenol, may be converted into a potentially reactive, brittle, transparent resin. Baekeland<sup>18</sup> heated, for example, 100 parts of dihydroxydiphenylethane with 10 parts of paraform or 12 parts of hexamethylenetetramine first at about 180°C. and later at 200°C. until a resin which solidified on cooling was obtained.

Matheson<sup>19a</sup> effected the reaction of phenol and acetaldehyde at 50-80°C. under pressure in the presence of less than 1 per cent of a condensing agent comprising a halogen derivative of a non-metal, as phosphorus oxychloride, acetyl chloride, benzyl chloride or the chlorides of sulphur.

#### BUTYRALDEHYDE

A resin was prepared by Ellis<sup>19</sup> by heating phenol and butyraldehyde with concentrated hydrochloric acid. A soft viscous brown substance was formed, which hardened considerably on heating. Furfural, with potassium carbonate as a catalyst, as well as hexamethylenetetramine, served to harden the product, which was adaptable for hot and cold molding or for varnishes, adhesives and impregnants. A related procedure is described by Schrimpe.<sup>20</sup>

#### BENZALDEHYDE

Gluud and Breuer<sup>21</sup> obtained fusible dark brown resins soluble in alcohol, benzene and aqueous solutions of alkali by condensing benzaldehyde with phenol

<sup>15</sup> German P. 426,866, 1923, to Progress A-G; *Brit. Chem. Abs.* B, 1926, 889

<sup>16</sup> Carleton Ellis, U. S. P. 1,974,605, Sept. 25, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 7563. See also U. S. P. 1,500,303, July 8, 1924; *Chem. Abs.*, 1924, 18, 2817.

<sup>17</sup> L. H. Baekeland and A. H. Gotthelf, U. S. P. 1,598,546, Aug. 31, 1926, to Bakelite Corp.; *Chem. Abs.*, 1926, 20, 3581.

<sup>18</sup> L. H. Baekeland, U. S. P. 1,637,512, Aug. 2, 1927; *Chem. Abs.*, 1927, 21, 3137. French P. 634,925, 1927; *Chem. Abs.*, 1928, 22, 4844. British P. 295,442, 1927, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 2309. German P. 525,494, 1927; *Chem. Abs.*, 1931, 25, 4139. See also Canadian P. 228,557, 1922; *Chem. Abs.*, 1923, 17, 1696.

<sup>19a</sup> H. W. Matheson, U. S. P. 1,653,302, Dec. 20, 1927, to Canadian Electro Products Co.; *Chem. Abs.*, 1928, 22, 849.

<sup>19</sup> Carleton Ellis, U. S. P. 1,477,870, Dec. 18, 1923; *Chem. Abs.*, 1924, 18, 760

<sup>20</sup> C. F. Schrimpe, U. S. P. 1,667,872, May 1, 1928, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 2282

<sup>21</sup> W. Gluud and P. K. Breuer, *Ges. Abhandl. Kennt. Kohle*, 1919, 4, 221; *Chem. Abs.*, 1921, 15, 3550.

or cresols. Fifty parts of phenol, 53 parts of benzaldehyde and 2 parts of ammonium chloride were heated for 7 hours on an oil bath at 120°C. Coatings obtained from a spirit varnish made with this resin were somewhat soft. Michael<sup>22</sup> also studied the formation of resinous bodies from benzaldehyde and phenols.

In a process used by Novotny and Romieux<sup>23</sup> the reaction of phenol with benzaldehyde is carried out in such a manner that the water liberated during condensation is removed almost immediately after it is formed. The product was hardened by heating with small quantities of inorganic acids, acid salts or methylene-engendering bodies.

According to Driver,<sup>24</sup> o- and p-hydroxybenzaldehyde do not react with phenol in the presence of sodium or potassium hydroxide, but on refluxing with concentrated hydrochloric acid, resins are secured in good yields.

From a study of the derivatives of p-nitrobenzaldehyde, King and Lowy<sup>25</sup> concluded that this substance may be condensed with two molecular equivalents of phenol, resorcinol, thymol, o-nitrophenol or o-methylanisole to yield amorphous solids

An essential oil having an aldehyde base, e.g., oil of cassia, oil of cinnamon or vanillin, was treated with a phenolic compound by McIntosh<sup>26</sup> to give a fusible, soluble resin which by further heating could be transformed into a hard, infusible product. One hundred grams of oil of cassia, for example, were digested under reflux for about 2 hours with 200 g of phenol and 2-5 g. of sulphuric or hydrochloric acid. The material obtained was shiny, hard, black, and sweet-smelling and was reported to be suitable as a varnish or shellac substitute.

A resin, stated to give water-resistant, elastic films, has been formed by the condensation of phenols with the oxidation products of certain hydrocarbons.<sup>27</sup> Saturated or unsaturated hydrocarbons with a chain of 2-6 carbon atoms (such as ethylene and other gaseous products from the cracking of oils) are oxidized by heating at 400-700°C. in the vapor phase (using acid phosphates as catalysts) with 5-10 per cent of oxygen. The resulting yellow oil, containing various aldehydes, principally formaldehyde, and some aliphatic acids, alcohols and esters, is reacted with a phenol at 95-100°C. for 2-3 hours. After separating any water present, further heating under vacuum at the same temperature for 2 hours yields a resin which is fusible, but which can be hardened to an infusible bubble-free mass by an additional 12-hour heating.

#### ACETYLENE

Wenzke and Nieuwland<sup>28</sup> studied the catalytic condensation of acetylene with phenol, the cresols, the naphthols, resorcinol and hydroquinone, pyrogallol and phloroglucinol, and various substituted phenols. Resorcinol and acetylene yielded ethylidene dioresorcinol with linkage ortho and para, respectively, to the two hydroxyl groups. This compound then lost a molecule of water to form dihydroxymethylxanthene. The catalysts used consisted of mercury salts in concentrated sulphuric acid. It was stated that phenol absorbed acetylene very readily, but the product formed did not have the properties of the ethylidene diphenol (dihydroxydiphenylethane) prepared from acetaldehyde and phenol by the method

<sup>22</sup> A. Michael, *Am. Chem. J.*, 5, 333. See Chapter 13

<sup>23</sup> E. E. Novotny and C. J. Romieux, U. S. P. 1,738,310, Dec. 3, 1929, to J. S. Stokes; *Chem. Abs.*, 1930, 24, 981.

<sup>24</sup> J. E. Driver, *J.S.C.I.*, 1927, 46, 197.

<sup>25</sup> C. G. King and A. Lowy, *J.A.C.S.*, 1924, 46, 757. See also P. Danckwortt, *Ber.*, 1909, 42, 4163

<sup>26</sup> J. McIntosh, U. S. P. 1,679,322, July 31, 1928, to Diamond State Fibre Co.; *Chem. Abs.*, 1928, 22, 3792.

<sup>27</sup> French P. 735,906, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1221.

<sup>28</sup> H. H. Wenzke and J. A. Nieuwland, *J.A.C.S.*, 1924, 46, 177.

of Claus and Trainer.<sup>20</sup> This seemed especially striking since the same catalysts (mercury salts) can be employed to convert acetylene to acetaldehyde.<sup>20</sup> In a later work, Nieuwland and Flood<sup>21</sup> reported that acetylene and acetaldehyde are probably alike in their reaction with phenols. The primary reaction product of the catalytic condensation of acetylene and resorcinol, as well as of acetaldehyde and resorcinol, was identified as vinyl resorcinol.<sup>22</sup>

Matheson and Nieuwland<sup>23</sup> passed dry acetylene into phenol or cresol containing 2.1-4.0 per cent of mercurous sulphate and 1-2 per cent of sulphuric acid at 90-115°C. until approximately 14 per cent of acetylene was absorbed. Glacial acetic acid served as a solvent and the temperature was raised to 120-150°C. at the end of the operation. The product may be combined with aldehydic hardening agents and rendered infusible

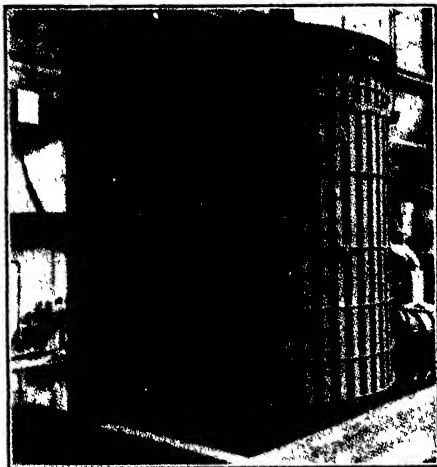


Fig. 66.  
Reinforced Haveg Apparatus.

Courtesy Haveg Corporation

and insoluble by heating under pressure. The use of other hydrocarbons containing a triple bond was suggested. Matheson and Skirrow<sup>24</sup> described a process of treating a soluble fusible acetylene-phenol compound with aldehydes and other hardening agents to transform it to the infusible insoluble stage. Thus, an acetylene-phenol resin is treated with less than 35 per cent of acetaldehyde and then hexamethylenetetramine is added. When over 35 per cent of acetaldehyde is employed, generally no additional agent is necessary. The product can be used in molding materials or as a varnish.<sup>25</sup>

According to Melamid,<sup>26</sup> if acetylene is admitted for a considerable period of time into a mixture of cresols (in the presence of sulphuric acid and a mercury salt as catalyst) and the latter then is submitted to a vacuum distillation, a high-boiling distillate is obtained, which is completely soluble in water when sul-

<sup>20</sup> A. Claus and E. Trainer, *Ber.*, 1886, 19, 3009. See Chapter 13

<sup>20</sup> H. W. Matheson, British P. 132,557, 1918; *Chem. Abs.*, 1920, 14, 288. U. S. P. 1,384,842, July 19, 1921; *Chem. Abs.*, 1922, 16, 2518. Reissue 15,434, Aug. 22, 1922; *Chem. Abs.*, 1922, 16, 2518. Canadian P. 218,373, 1922; *Chem. Abs.*, 1922, 16, 3685. R. R. Vogt and J. A. Nieuwland, *J.A.C.S.*, 1921, 43, 2071

<sup>21</sup> J. A. Nieuwland and S. A. Flood, *J.A.C.S.*, 1928, 50, 2566.

<sup>22</sup> Acetylene also condenses with benzene hydrocarbons in the presence of mercury catalysts. See J. S. Reichert and J. A. Nieuwland, *J.A.C.S.*, 1923, 45, 3090. J. A. Reilly and J. A. Nieuwland, *J.A.C.S.*, 1928, 50, 2564.

<sup>23</sup> H. W. Matheson and J. A. Nieuwland, U. S. P. 1,707,940, -41, April 2, 1929; *Chem. Abs.*, 1929, 23, 2585. British P. 227,216 and 232,277, 1923, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1925, 19, 2752, 3605. See also J. A. Nieuwland, British P. 183,830, 1922, to Shawmigan Laboratories, Ltd.; *J.S.C.I.*, 1924, 43, 265B.

<sup>24</sup> H. W. Matheson and F. W. Skirrow, U. S. P. 1,788,722, Jan. 13, 1931, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1931, 25, 1109. See also H. W. Matheson and J. A. Nieuwland, Canadian P. 250,295, 1925. J. S. Reichert and J. A. Nieuwland, *J.A.C.S.*, 1923, 45, 3090.

<sup>25</sup> H. W. Matheson, U. S. P. 1,650,899, Nov. 29, 1927, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1928, 22, 691. Canadian P. 262,391, 1926; *Chem. Abs.*, 1926, 20, 3580.

<sup>26</sup> M. Melamid, U. S. P. 1,710,266, April 23, 1929, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1929, 23, 2842. British P. 163,679, 1920; *J.S.C.I.*, 1922, 41, 261A.



phonated. This exhibited the properties of a tanning agent. The distillation residue is a hard, transparent resin soluble in alcohol and benzene.

Melamid gives the following procedure: Two hundred parts by weight of commercial cresol are added with cooling to about 40 parts of 50 per cent sulphuric acid, 5 parts of mercuric sulphate and 1 part of ferric chloride. A slow current of acetylene is admitted with stirring for a period of about 12 hours at room temperature. The resulting viscous mass is dissolved in benzene, separated from the catalyst by filtration and washing with water, dried and submitted to fractional distillation under a pressure of 8 mm. Up to 100°C. benzene and cresols pass over together, and between 100-200° a liquid product is obtained, leaving behind the resin described above.

In an analogous procedure<sup>37</sup> crude phenol or cresol is added to a solution of mercuric oxide in 30 per cent sulphuric acid and acetylene is passed into the vigorously stirred mixture. When the absorption is complete, the viscous reaction product is separated from the aqueous solution and washed. Excess phenol is driven off by steam and the mercury is eliminated by treatment with alcohol or benzene. A transparent residue, melting at about 100°C., was found to be soluble in sodium hydroxide but not in sodium carbonate. If phenolsulphonic acid is used instead of phenol, the condensation product is soluble in water and is said to be useful as a tanning material.

A permanently fusible acetylene-phenol-aldehyde resin is described by Novotny and Kendall.<sup>38</sup> This is made by heating a phenol-acetylene resin with 0.5 per cent of sulphuric acid in an autoclave to a temperature of about 125°C. and gradually adding up to about 8 per cent of paraldehyde with further increase of temperature and pressure. The acid is then neutralized and the resinous bodies removed. The material was stated to resemble shellac in its properties. A better grade of resin was secured by treatment with steam. Infusible products were obtained by heating the resin with hexamethylenetetramine at 90-200°C.

Methods of preparing soluble fusible acetylene-phenol compounds have been discussed by Schrimpe.<sup>39</sup> He treated 2.2 kg. of phenol, 880 cc. of water, 220 g. of concentrated sulphuric acid, and 45 g. of mercuric sulphate with acetylene. Additional mercuric sulphate tends to further activate the reaction. Schrimpe stated that the resin is of the type prepared by Baekeland and Gotthelf<sup>40</sup> from phenol and acetaldehyde, and that the first reaction product is probably vinyl sulphuric acid,  $\text{CH}_2=\text{CHSO}_3\text{H}$ , which reacts with phenol to form ethylidene diphenol (dihydroxydiphenylethane).

A modified catalyst consists of a porous substance, e.g., kieselguhr or wood charcoal, impregnated with a solution of mercuric oxide in sulphuric acid. This mass is introduced into a solution of phenol in benzene and the mixture is treated with acetylene.<sup>41</sup>

The material obtained by condensing phenols with acetylene under pressure at 100-300°C. in the presence of an organic base, instead of treatment with aldehydes, may be sulphonated to yield tanning agents, esterified with polybasic organic acids, or condensed with ethylene oxide to give water-soluble ethers.<sup>42</sup>

In place of mercury salts, the use of zinc or cadmium salts of acetic or other organic acids has been suggested.<sup>43</sup> No sulphuric acid is needed with this type of catalyst, the acetylene being introduced into phenol, cresol, o-chlorophenol, resorcinol and similar substances at 100-300°C. Reaction is usually carried out at 5-10 at-

<sup>37</sup> German P. 422,904, 1914, to Chem. Fabr. Gustrow, Hillringhaus and Heilmann; *Brit. Chem. Abs.* B, 1926, 596.

<sup>38</sup> E. E. Novotny and D. S. Kendall, U. S. P. 1,470,637, Oct. 16, 1924, to J. S. Stokes; *Chem. Abs.*, 1924, 18, 175.

<sup>39</sup> C. F. Schrimpe, U. S. P. 1,742,519, Jan. 7, 1930, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 1125.

<sup>40</sup> L. H. Baekeland and A. H. Gotthelf, U. S. P. 1,598,546, Aug. 31, 1926; *Chem. Abs.*, 1926, 20, 3581. See section on acetaldehyde-phenol resins in this chapter.

<sup>41</sup> German P. 523,993, 1924, to A.-G. für Chemiewerte; *Chem. Abs.*, 1931, 25, 3856. C. Stein, French P. 678,283, 1929; *Chem. Abs.*, 1930, 24, 3662.

<sup>42</sup> British P. 413,640, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1934, 826.

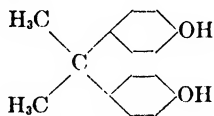
<sup>43</sup> British P. 407,997, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1934, 591. French P. 758,042, 1934; *Chem. Abs.*, 1934, 28, 3255.

mospheres pressure under nitrogen. With phenol a clear resin (m.p. 100-130°C) was obtained, which could be hardened by hexamethylenetetramine or esterified with linoleic acid to form a soft, alkali-soluble resin. Darker resins resulted when resorcinol, diphenylpropane and o-chlorophenol were used.

#### ACETONE AND OTHER KETONES

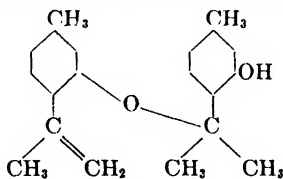
Condensation products of phenol and acetaldehyde, as previously mentioned, have a tendency to be crystalline. Compounds made by the interaction of acetone and phenol exhibit this tendency to a still greater degree. Usually 4,4'-dihydroxydiphenyldimethylmethane is formed first, this is separated and purified, and then reacted with additional acetone. Or a more reactive aldehyde (as formaldehyde) is used to give resinous products.

Dianin<sup>44</sup> prepared 4,4'-dihydroxydiphenyldimethylmethane (p-diphenyldimethylmethane) by heating 220 g. of acetone with 1600 g. of phenol, 1800 cc. glacial acetic acid and 600 cc. hydrochloric acid (sp.gr. 1.19) at 40-50°C. for several days in a bomb. The compound

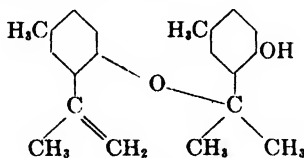


crystallized as needles or prisms, having a melting point of 151-152° and could be recrystallized from water. Arvin<sup>45</sup> states that by using an acid-soluble boron compound such as boric acid in conjunction with an acid condensing agent such as hydrochloric, or sulphuric acid, the yields of p-phenyldimethylmethane are increased and purer products result.

Jordan<sup>46</sup> condensed m- and p-cresol with acetone, using hydrochloric acid, phosphorus oxychloride or metallic halides at temperatures up to 100°C, and obtained dimer products, useful as disinfectants and deodorants. The material derived from m-cresol was considered to have the formula



and that from p-cresol was thought to be



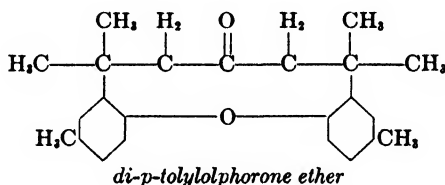
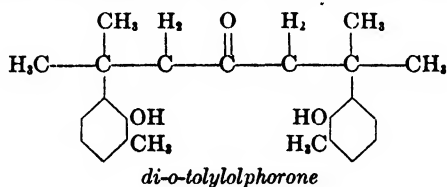
<sup>44</sup> A. Dianin, *J. Russ. Phys.-Chem. Soc.*, 1901, 23, 499; *Ber.*, 1892, 25, 334R.

<sup>45</sup> J. A. Arvin, U. S. P. 1,986,423, Jan. 1, 1935, to E. I. du Pont de Nemours & Co; *Chem. Abs.*, 1935, 29, 1103.

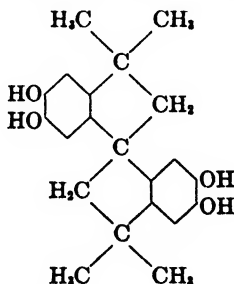
<sup>46</sup> H. Jordan, U. S. P. 1,854,940, April 19, 1932, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1932, 26, 3335. *British P.* 273,684 and 308,741, 1927; *Chem. Abs.*, 1929, 23, 1911; 1930, 24, 382. *German P.* 484,768, 1926; *Chem. Abs.*, 1930, 24, 2256. *French P.* 645,271, 1927; *Brit. Chem. Abs. B.*, 1929, 236. See also U. S. P. 1,690,769, Dec. 25, 1928; to Chem. Fabr. E. Schering A.-G.; *Chem. Abs.*, 1929, 23, 852. *British P.* 279,856, 1927; *Chem. Age (London)*, 1928, 17, 14. *Swiss. P.* 127,522, 1927; *Chem. Abs.*, 1929, 23, 1139. Also *British P.* 293,863, 1928; *Brit. Chem. Abs. B.*, 1929, 636. Also U. S. P. 1,961,397, June 5, 1934; *Chem. Abs.*, 1934, 28, 4848.

When a mixture of m- and p-cresols was used, the products were separated by fractional crystallization from ether, the m-cresol derivative crystallizing while the p-cresol form remained in the mother liquor. The former melts at 73-75°C. and boils at 187°C., the latter boils at 192° (0.8 mm. mercury). Condensations were made also with methyl ethyl ketone and cyclohexanone and resulted in compounds of related structure. The vacuum-distilled products solidified on cooling to clear or light-yellow amorphous masses.

Niederl and Casty<sup>47</sup> conducted an extensive study of the structure of acetone-cresol compounds, and proposed a number of formulas. They stated that if a mixture of o-cresol and acetone or phorone is treated with cold concentrated sulphuric acid there results a condensation product which may be termed di-o-tolylol-phorone (m.p. 245°C.). This gives sodium and potassium salts when treated with alcoholic alkali hydroxide solution. Similarly p-cresol and acetone furnishes di-p-tolylolphorone ether (m.p. 137°). The constitution of di-m-tolylolphorone ether follows from the production of thymol, menthol and trimethylcoumarone from it, by successive oxidation, elimination of carbon dioxide or water, and hydrogenation.



Gsell<sup>48</sup> reported producing solid substances by boiling 50 cc. of acetone and 50 g. of resorcinol with 3-5 cc. of strong hydrochloric acid. A colorless, finely crystalline substance (m.p. 315°) was secured by Baker<sup>49</sup> by refluxing 2 mols of catechol with 3 mols of acetone for 48 hours in a mixture of acetic acid and concentrated hydrochloric acid. This was considered to be 5,6,5',6'-tetrahydroxy-3,3,3',3'-tetramethylbis-1,1'-spirohydrindene and to have the following structural formula



<sup>47</sup> J. B. Niederl, *J.A.C.S.*, 1928, 50, 2230. J. B. Niederl and R. Casty, *Monatsh.*, 1929, 51, 86; *Brit. Chem. Abs. A*, 1929, 551. J. B. Niederl, *Monatsh.*, 1932, 60, 150; *Brit. Chem. Abs. A*, 1932, 842. See also British P. 273,684, 279,886 and 279,887, 1929, to Schering-Kahlbaum A.-G.; *Brit. Chem. Abs. B*, 1929, 237, 316.

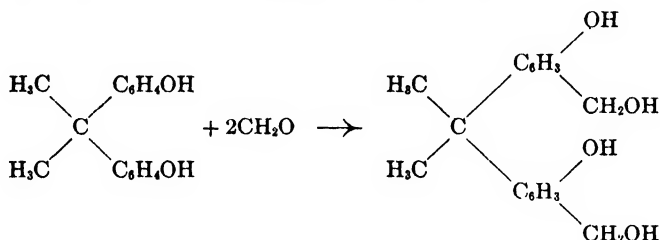
<sup>48</sup> J. Gsell, *Chem.-Ztg.*, 1914, 38, 541; *J.S.C.I.*, 1914, 33, 875.

<sup>49</sup> W. Baker, *J.C.S.*, 1934, 1678.

It is believed that the 3 mols of acetone first unite to form phorone, which in turn condenses with the catechol. This was borne out by the fact that substitution of phorone for acetone in the preparation resulted in a similar end-product.

A procedure for the preparation of dihydroxydiphenyldimethylmethane (m.p. 150-154°C.) has been given by Beatty.<sup>50</sup> A mixture of 840 parts by weight of phenol, 175 parts of acetone and 74 parts of hydrochloric acid (sp.gr. 1.20) is allowed to stand at 30-40° until the entire mixture becomes solid. The crystals thus produced are washed with dilute acetic acid and, if necessary, recrystallized from water or dilute acetic acid and dried. To form a resin from this compound, 228 parts are then dissolved in 60 parts of hot 40 per cent formaldehyde solution and 2.28 parts of sodium hydroxide are added. The mixture is heated to 100°C. until the reaction proceeds to completion. A brittle resin is obtained, soluble in acetone, alcohol, amyl alcohol, amyl acetate, acetylene tetrachloride and strong alkali. Acidification of the alkaline solution gives a resin which is insoluble in alkali, linseed oil, turpentine and mineral oils. Longer heating produces a material insoluble in all solvents.

The reactions, according to Beatty,<sup>51</sup> are as follows:



Two molecules of this product then condense (the hydrogen of the phenolic hydroxyl uniting with the hydroxyl of the carbinol group) with the splitting out of water. Acids, alkalis or acid or basic salts may be used as catalysts. The process is varied by using other ketones in place of acetone and cresols instead of phenol.<sup>52</sup> Camphor, acetanilide, triphenylphosphate or alkyl derivatives of the benzenesulphonamides may be incorporated as plasticizers.<sup>53</sup> The products are intended for a variety of uses,<sup>54</sup> e.g., in varnishes,<sup>55</sup> in cellulose acetate compositions<sup>56</sup> for artificial silk filaments and fabrics made therefrom,<sup>57</sup> in films,<sup>58</sup> as a coating for films<sup>59</sup> or for the manufacture of sound records.<sup>60</sup>

A phenol-ketone resin made by McIntosh<sup>61</sup> was suggested for use in electrical insulation. Phenol and acetone or methyl ethyl ketone may be boiled under reflux with a catalyst (sulphuric acid, bromine, pyridine) until a gummy mass results. This is further heated at 120-130°C. to a shellac-like solid and then dissolved in a solvent (e.g., acetone or alcohol). Hexamethylenetetramine (5 per cent) is added and the solvent is removed by distillation. The resulting material is subjected to heat and pressure to convert it into an infusible form. Ketone-phenol

<sup>50</sup> W. A. Beatty, U. S. P. 1,225,748, May 15, 1917; *Chem. Abs.*, 1917, 11, 2142.

<sup>51</sup> W. A. Beatty, U. S. P. 1,156,969, Oct. 19, 1915; *Chem. Abs.*, 1915, 9, 3358. U. S. P. 1,225,748, 1,225,749, 1,225,750, Oct. 19, 1915, to G. W. Beadle; *Chem. Abs.*, 1917, 11, 2142, 2143, 2144. French P. 447,647, 1912; *J.S.C.I.*, 1913, 32, 244. British P. 18,824, 1912; *Chem. Abs.*, 1914, 8, 585.

<sup>52</sup> W. A. Beatty, U. S. P. 1,158,962, Nov. 2, 1915; *Chem. Abs.*, 1916, 8, 278.

<sup>53</sup> W. A. Beatty, U. S. P. 1,188,356, June 20, 1916; *Chem. Abs.*, 1916, 10, 2146.

<sup>54</sup> C. W. Rivise (*Plastics*, 1924, 4, 429; *Chem. Abs.*, 1928, 24, 4209) has compiled the information from the W. A. Beatty patents in an article on dihydroxydiphenyldimethylmethane (diphenylolpropane). Its preparation and applications are discussed.

<sup>55</sup> W. A. Beatty, U. S. P. 1,113,926, Oct. 13, 1914; *Chem. Abs.*, 1914, 8, 3866.

<sup>56</sup> W. A. Beatty, U. S. P. 1,158,960, Nov. 2, 1915; *Chem. Abs.*, 1916, 10, 275.

<sup>57</sup> W. A. Beatty, U. S. P. 1,156,969, Oct. 19, 1915; *Chem. Abs.*, 1915, 9, 3358.

<sup>58</sup> W. A. Beatty, U. S. P. 1,158,961, Nov. 2, 1915; *Chem. Abs.*, 1916, 10, 275.

<sup>59</sup> W. A. Beatty, U. S. P. 1,158,968, Nov. 2, 1915; *Chem. Abs.*, 1916, 10, 158.

<sup>60</sup> W. A. Beatty, U. S. P. 1,158,964, Nov. 2, 1915; *Chem. Abs.*, 1916, 10, 257.

<sup>61</sup> J. McIntosh, U. S. P. 1,448,556, Mar. 13, 1923, to Diamond State Fiber Co.; *Chem. Abs.*, 1923, 17, 1852.

resins are said to form hard, resistive, odorless, lightproof bodies when mixed with such filling materials as chalk, dolomite, magnesia, alumina, metal oxides, asbestos, cellulose, wood or wool.<sup>62</sup>

Liquid resinous substances soluble in dilute alkalies were obtained by Amann and Fonrobert<sup>63</sup> on treating a hydroxyarylmethane (derived from the condensation of a ketone and a phenol) with an aldehyde in alkaline medium at 60-80°C. The resin, precipitated by addition of acid, was transformed into an insoluble infusible form by heating.

Terwilliger<sup>64</sup> recommended condensing a coal-tar fraction, boiling between 184-224°C., with an aldehyde, using an alkaline catalyst. Acetone, or light or heavy acetone oil, may be employed simultaneously. For example, a resin was prepared from 100 parts of coal-tar oil (b.p. 184-224°C.), 30 parts of acetone, 50 parts of paraformaldehyde and 3 parts of sodium hydroxide. The degree of condensation is regulated by the temperature to which the mixture is heated or by the duration of heating.

Walker<sup>65</sup> treated a phenol first with an aliphatic ketone and then with an aliphatic aldehyde, either or both reactions being carried out with alkaline catalysts. A white crystalline product was formed if, after the second step, acid was added to bring the  $p_H$  value to about 6. The product from phenol, acetone and formaldehyde had a melting point of 123-127°C.

Moss<sup>66</sup> used equimolecular proportions of phenol and acetone with hydrochloric, boric, phosphoric or sulphuric acid as catalysts to yield a resinous substance soluble in benzene, acetone and alcohol. The reaction was described as taking place in two stages; first, the formation of diphenylolpropane, recalling the product obtained by Dianin<sup>67</sup> and second, combination with the remaining acetone to give the resin. Diphenylolpropane (dihydroxydiphenyldimethylmethane) may also be condensed with ketones other than acetone, e.g., methyl ethyl ketone, diethyl ketone or chloracetone or with aldehydes. A direct union of 1 mol of diphenylolpropane with less than 2 mols of an aldehyde may also be made. For example when formaldehyde is used and condensation carried out at 110-130°C., a resin is formed with a melting point of 140-150°. Moreover, it can be heated to this temperature for a considerable time without overcondensation, thus permitting the unreacted substances to be driven off. The diphenylolpropane resins in general are said to be adaptable for use with cellulose esters and ethers in lacquers and adhesives, including cements for laminated glass. Diphenylolpropane<sup>68</sup> may be replaced by diphenylol-cyclohexane, this being accomplished by substituting cyclohexanone for acetone in the initial reaction.

The crude products obtained by the interaction of phenol with ketones were treated with a solution of an alkali or alkaline earth. The slightly soluble salt

<sup>62</sup> German P. 527,866, 1921, to Chem. Fabrik. K. Albert G m b H.; *Chem. Abs.*, 1931, 25, 5259. See also German P. 494,778, 1921; *Chem. Abs.*, 1930, 24, 3615.

<sup>63</sup> A. Amann and E. Fonrobert, U. S. P. 1,614,172, Jan. 11, 1927, to Chem. Fabr. Dr. K. Albert G m b H.; *Chem. Abs.*, 1927, 41, 805. British P. 261,522, 1925; *Chem. Abs.*, 1927, 21, 3474. German P. 494,778, 1921; *Chem. Abs.*, 1930, 24, 3615. See also German P. 527,866, 1921; *Chem. Abs.*, 1931, 25, 5259.

<sup>64</sup> C. O. Terwilliger, U. S. P. 1,624,638, April 12, 1927; *Chem. Abs.*, 1927, 21, 1890. British P. 218,638, 1923; *ibid.*, 1925, 19, 581. Canadian P. 258,978, 1926; *ibid.*, 1926, 20, 2420. See also British P. 218,277, 1923; *Chem. Abs.*, 1925, 19, 581.

<sup>65</sup> E. E. Walker, British P. 298,680, 1927, to British Dvestuffs Corp., Ltd.; *Chem. Abs.*, 1929, 23, 3060.

<sup>66</sup> W. H. Moss, U. S. P. (all to Celanese Corp. of America) 1,848,644, Mar. 8, 1932; 1,878,249, Sept. 20, 1932; 1,920,100, July 25, 1933; 1,923,111, Aug. 22, 1933; 1,929,209, Oct. 3, 1933; 1,929,559, Oct. 10, 1933; 1,958,488, May 15, 1934; *Chem. Abs.*, 1932, 26, 3125; 1933, 27, 435, 4944, 5168, 5753; 1934, 28, 89, 4616. British P. (to Brit. Celanese, Ltd.) 299,065 to 299,067, 1927; *Chem. Abs.*, 1929, 23, 3115; 342,429, 1929; *Brit. Chem. Abs. B.*, 1931, 405; 342,674, 1929; *Brit. Chem. Abs. B.*, 1931, 598; 366,586, 1929; *Brit. Chem. Abs. B.*, 1931, 452; 369,294, 1930; *Chem. Abs.*, 1933, 27, 3045; 401,299, 1933; *Chem. Abs.*, 1934, 28, 2489 and 409,896, 1933; *Brit. Chem. Abs. B.*, 1934, 592. Canadian P. 319,730, 319,731 and 319,732, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 2609.

<sup>67</sup> A. Dianin, *loc. cit.*

<sup>68</sup> For further information on the formation of diphenylolpropane see R. Greenhalgh, U. S. P. 1,977,627, Oct. 23, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 181. British P. 395,732, 1933; *Chem. Abs.*, 1934, 28, 492. Also S. Kohn and E. Schub, U. S. P. 1,978,949, Oct. 30, 1934, to Rohm & Haas Co., Inc.; *Chem. Abs.*, 1935, 29, 181.

which formed could then be separated, according to Koch and Guthke,<sup>66</sup> from the readily soluble phenolate derived from excess phenol in the reaction mixture.

Schuch<sup>70</sup> recommended mixing fusible condensation products from phenol and formaldehyde with cyclohexanone in an amount sufficient to combine with any free phenol and formaldehyde. A heat-hardening resin resulted. Braun, Anton, Haensel and Werner<sup>71</sup> obtained resinous products through the reaction of cyclohexanone with phenol and m-cresol, using hot hydrochloric acid. Diphenylolpropane-formaldehyde resin has been suggested for use in a cellulose acetate composition for coating rubber-insulated cables.<sup>72</sup> Irey formed the condensation product of a phenol and a ketone and treated it with formaldehyde in amounts of 0.1-0.4 mols for each mol of phenol in the initial reaction. By this means he secured a resin soluble in ordinary drying oils.<sup>73</sup> Hill and Walker<sup>74</sup> used o-cresol with ketones and aldehydes to give a similar product. Kraus<sup>75</sup> condensed phenol, acetone and formaldehyde with an alkaline catalyst to obtain resins that could be hardened by heat and pressure. A similar procedure is described by Süssenguth,<sup>76</sup> who further treats the resin with an acid (citric, phosphoric) to secure a heat-hardenable substance. He considers that diphenylolpropane formation does not take place in this case, but that a different type of material is synthesized. Finkelstein<sup>77</sup> and Steimmig<sup>78</sup> found that cyclic ketone resins are compatible with nitrocellulose, dissolving readily in glycol ethers, e.g., ethylene glycol methyl ether, and their esters.<sup>79</sup>

Mixtures of aromatic hydroxy compounds and cyclic ketones were heated with aldehydes in the presence of condensing agents by Schmidt and Seydel.<sup>80</sup> Resins were produced from phenol, cresol or  $\alpha$ -naphthol, cyclohexanone or methylcyclohexanone and 30 per cent formaldehyde, benzaldehyde or paraldehyde. Seydel and Roh<sup>81</sup> dissolved a mixture of phenol and cyclohexanone in benzene and subjected it to a current of dry hydrogen chloride. Bis-p-hydroxyphenyl-1,1-cyclohexane was formed and this compound, when dissolved in alcohol and treated with formaldehyde and concentrated hydrochloric acid, yielded a resin-like product melting at 180-200°C.

Mixtures of cyclic ketones and aromatic or hydroaromatic hydroxy compounds (e.g., cyclohexanol or phenol) may be condensed<sup>82</sup> in the presence of acid, alkaline or neutral condensing agents to obtain resins said to be stable to light, alkalies and acids, soluble in linseed oil and useful in the manufacture of lacquers.<sup>83</sup> A variety of products may be obtained by the condensation of phenols with  $\alpha$ - and  $\beta$ -unsaturated ketones.<sup>84</sup> With a phenol such as resorcinol, the yield is said to be almost quantitative. The substances formed varied in color with the different

<sup>66</sup> W. Koch and F. W. Guthke, German P. 604,406, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 855.

<sup>70</sup> K. A. Schuch, German P. 567,072, 1930, to Aug. Nowack A.-G.; *Chem. Abs.*, 1933, 27, 1464.

<sup>71</sup> J. von Braun, E. Anton, W. Haensel and G. Werner, *Ann.*, 1929, 472, 1; *Brit. Chem. Abs. A.*, 1929, 1059.

<sup>72</sup> H. Dreyfus, British P. 407,709, 1934; *Chem. Abs.*, 1934, 28, 5263.

<sup>73</sup> K. M. Irey, U. S. P. 1,948,469, Feb. 20, 1934, and 1,970,912, Aug. 21, 1934, to Resinox Corp.; *Chem. Abs.*, 1934, 28, 2928, 6330.

<sup>74</sup> A. Hill, R. Hull and E. E. Walker, British P. 401,309, 1932, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B.*, 1934, 71.

<sup>75</sup> W. Kraus, Austrian P. 135,858, 1933; *Chem. Abs.*, 1934, 28, 2556.

<sup>76</sup> O. Süssenguth, U. S. P. 1,989,951, Feb. 5, 1935, to Bakelite G.m.b.H.; *Chem. Abs.*, 1935, 29, 1904.

<sup>77</sup> H. Finkelstein, U. S. P. 1,801,340, April 21, 1931 and 1,812,145, June 30, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3502, 5048.

<sup>78</sup> G. Steimmig, U. S. P. 1,883,060, Oct. 18, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 857.

<sup>79</sup> A discussion of mixtures of synthetic resins and cellulose esters is found in Chapter 63.

<sup>80</sup> O. Schmidt and K. Seydel, German P. 407,668, 1922, to Badische Anilin- & Soda-Fabr., *J.S.C.I.*, 1925, 44, 461B.

<sup>81</sup> K. Seydel and N. H. Roh, German P. 484,739, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1236.

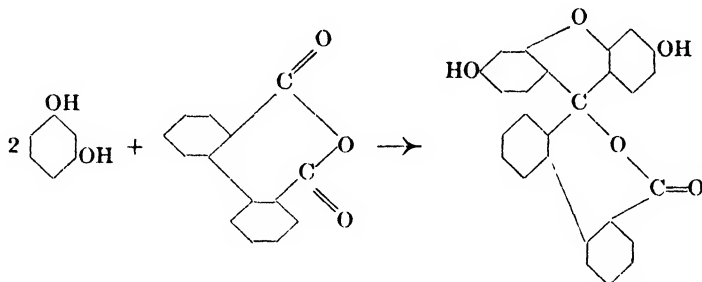
<sup>82</sup> British P. 276,518, 1926, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1927, 851.

<sup>83</sup> E. Korten (German P. 467,738, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 1729. French P. 647,464, 1928; *Chem. Abs.*, 1929, 23, 2540) condensed phenols with hydroaromatic ketones in the presence of a halogen hydrosol to obtain products useful as dye or drug intermediates.

<sup>84</sup> German P. 357,755, 1923, to Chem. Fabrik. vorm. Weilerter Meer; *Chem. Abs.*, 1923, 17, 2118.

constituents. For example, the compound from phenol and styryl methyl ketone is a gray powder, that from resorcinol and the same ketone is a yellow powder. Sen and Basu<sup>86</sup> studied the reaction between cyclohexanol-2-carboxylate and phenols. They found that ethyl cyclohexanone-2-carboxylate and resorcinol (with phosphorus pentoxide) yielded tarry resinous substances.

Diphenic anhydride and resorcinol, heated at 135-150°C. with zinc chloride, form an amorphous ruby red glass.<sup>87</sup> One reaction which is believed to take place is



According to Underwood and Clough,<sup>88</sup> this material contains resorcinoldiphenic and an amorphous condensation product derived from diphenyleneketone-4-carboxylic acid. Amorphous derivatives of the diphenic anhydrides from resorcinol and substituted diphenic anhydrides have also been described.<sup>89</sup>

#### UNSATURATED ALDEHYDES AND POLYHYDRIC ALCOHOLS

Resins can be made from phenols and unsaturated aldehydes. Acrolein,  $\text{CH}_2=\text{CHCHO}$ , is a dehydration product of glycerol,  $\text{CH}_2\text{OHCHOHCH}_2\text{OH}$ , and the two can, therefore, be logically considered in the same group. Darke and Lewis,<sup>90</sup> from a study of some of the resinification reactions of glycerol, conclude that the polyhydric alcohol is probably first converted to acrolein. Maksorov and Andrianov<sup>91</sup> report that when phenol and glycerol are condensed the glycerol appears to be first converted into acrolein and polyglycerides which then combine with phenol.<sup>91</sup> The condensations of phenol and unsaturated aldehydes such as acrolein, should therefore be considered first.

A hard, insoluble, non-conducting resin was produced by Moureu and Dufrasse<sup>92</sup> in a single operation by condensing phenol and acrolein with about 1 per cent of sodium hydroxide. Acrolein, they state, may be replaced by its polymerization products, for instance, a polymerized acrolein resin.<sup>93</sup> Kishi<sup>94</sup> reacted the aldehyde with phenol under 30 atmospheres pressure using as catalyst salts which give an acid reaction on being hydrolyzed (e.g., zinc chloride or aluminum chlo-

<sup>86</sup> H. K. Sen and U. Basu, *J. Indian Chem. Soc.*, 1928, 5, 467; *Chem. Abs.*, 1929, 23, 383.

<sup>87</sup> T. Bischoff and H. Adkins, *J.A.C.S.*, 1923, 45, 1030.

<sup>88</sup> H. W. Underwood, Jr. and L. A. Clough, *J.A.C.S.*, 1929, 51, 533.

<sup>89</sup> F. Steinberg, H. Adkins and E. Pickering, *J.A.C.S.*, 1924, 46, 1917. See also H. W. Underwood, Jr. and E. L. Kockman, *J.A.C.S.*, 1923, 45, 3071.

<sup>90</sup> W. F. Darke and E. Lewis, *J.S.C.I.*, 1923, 47, 1085.

<sup>91</sup> B. V. Maksorov and K. A. Andrianov, *Ind. Eng. Chem.*, 1932, 24, 827.

<sup>92</sup> The name "Acrolite" has been given to a resin made by J. McIntosh (*Ind. Eng. Chem.*, 1927, 19, 111) from phenol and glycerol. This name has taken on generic significance and would now probably include resins from phenol and acrolein also.

<sup>93</sup> C. Moureu and C. Dufrasse, *U. S. P.* 1,607,293, Nov. 16, 1926; *Chem. Abs.*, 1927, 21, 307. German P. 282,903, 1920; *Chem. Zentr.*, 1924, 1, 1715. British P. 141,059, 1920; *Chem. Abs.*, 1920, 14, 2270. French P. 528,498.

<sup>94</sup> British P. 141,058, 1920; *Chem. Abs.*, 1920, 14, 2270.

<sup>95</sup> N. Kishi, *Japanese P.* 79,157, 1929; see B. V. Maksorov and K. A. Andrianov, *Ind. Eng. Chem.*, 1932, 24, 827.

ride). From their work, Maksorov and Andrianov<sup>95</sup> concluded that the rate of condensation with an acid catalyst is at a maximum when 5 mols of acrolein to 1 mol of phenol are used, and with a basic catalyst when 25 mols of acrolein to 1 mol of phenol are employed. With an acid catalyst the rate of condensation is rapid at first, but slows up toward the end of the reaction, while with a basic catalyst the behavior is reversed. Xylenol-acrolein resins show a higher rate of conversion into an infusible and insoluble condition than do those from phenol and acrolein. They also have a higher melting point, as do the acrolein-cresol resins.

The use of other unsaturated aldehydes has been suggested also. For example, crotonaldehyde or aldol (which on distillation at atmospheric pressure loses water and becomes crotonaldehyde) or mixtures of both, can be reacted with phenols or nuclear methylated phenols or mixtures of these.<sup>96</sup> Polyhydric phenols, partially etherified, or creosote may be employed also. Mineral acids or compounds giving rise to hydrogen chloride (e.g., thionyl chloride) can be used as condensing agents. Carrying out the reaction in the cold gives rise to oils, while heating gives more resinous substances. Both types are soluble in most organic solvents and in caustic alkali, but are insoluble in alkali bicarbonate. The oily bodies dry in air, especially with drying agents, to films reported to be stable and weather-resistant. The product from phenol and aldol is a viscous oil having an iodine value of 130-160. A substitute for linseed oil is said to be derived from crotonaldehyde and creosote.

The oily materials can be treated with formaldehyde and condensing agents<sup>96a</sup> to yield more viscous though soluble forms, which can be rendered infusible and insoluble by heating under pressure. Balle and Wohlers<sup>97</sup> suggested that the acid-catalyzed condensation products of phenols with aldol or crotonaldehyde are adaptable for the production of oil varnishes. Steindorff and Balle<sup>97</sup> also combined resins of this type, while still soluble and fusible, with phenol formaldehyde resins to form insoluble and infusible compounds.<sup>98</sup> Herrmann and Deutsche<sup>99</sup> used crotonaldehyde together with polyphenols, such as resorcinol or pyrogallol, to prepare resinous materials.

A resin from phenol and glycerol is described by McIntosh.<sup>100</sup> It is said to possess a high luster and excellent heat-resisting qualities and to have all the desirable properties of the phenol-formaldehyde type of resin. The resin is obtained, according to McIntosh and Wolford,<sup>101</sup> by boiling 100 g. of phenol and 90-100 g. of glycerol with about 20 drops of sulphuric acid under reflux for 6-8 hours. The liquid is then subjected to a temperature of about 125°C. for further condensation. After 5 hours heating at 125°C. the product is still fusible and is soluble in alcohol, acetone and benzene. Following about 24 hours at this temperature it is insoluble in all the mentioned solvents and is infusible. The resin can be used for practically the same purposes for which phenol-formaldehyde resins are employed. Hardening agents suggested include hexamethylenetetramine, benzidine-acetone and sodium-acetone-bisul-

<sup>95</sup> B. V. Maksorov and K. A. Andrianov, *loc. cit.*

<sup>96</sup> G. Balle and A. Steindorff, German P. 364,041 and 364,043, 1920, to Farb- u. vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1923, 42, 613A. See also B. V. Maksorov and K. A. Andrianov, *Rev. gen. mat. plast.*, 1933 9, 630, 683; *Chem. Abs.*, 1935, 29, 3068.

<sup>96a</sup> G. Balle, German P. 388,792, 1921, to Farb- u. vorm. Meister, Lucius & Brüning, *J.S.C.I.*, 1924, 43, 797B. G. Balle and A. Steindorff, German P. 388,795, 1922; *J.S.C.I.*, 1924, 43, 797B.

<sup>97</sup> G. Balle and H. Wohlers, German P. 406,153, 1922; *J.S.C.I.*, 1925, 44, 461B.

<sup>98</sup> A. Steindorff and G. Balle, German P. 479,161, 1922, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 4837.

<sup>99</sup> For a study of the condensation of aldehydes and ketones with o-aminothiophenols and benzothiazoles see H. P. Lankelma and P. X. Sharnoff, *J.A.C.S.*, 1932, 54, 379.

<sup>100</sup> W. O. Herrmann and H. Deutsche, German P. 523,695, 1928, to Consortium für Elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 3856.

<sup>101</sup> J. McIntosh, *Ind. Eng. Chem.*, 1927, 19, 111.

Also J. McIntosh and E. Wolford, U. S. P. 1,642,078, Sept. 13, 1927; *Chem. Abs.*, 1927, 21, 3756. Also J. McIntosh, U. S. P. 1,642,079, Sept. 13, 1927, to Diamond State Fiber Co.; *Chem. Abs.*, 1927, 21, 3756.



phite. To vary the procedure phenol is replaced by its homologues or substitution products and for glycerol epichlorhydrin, allyl alcohol, glycerol aldehyde, dihydroxyacetone can be substituted. Catalysts which have been found effective for the condensation include bromine, pyridine, sulphur monochloride and aniline hydrochloride.

A reaction product of glycerol and phenol was used by Coffey<sup>102</sup> as a binder for mica splittings. The resin is made by heating 100 g. of phenol, 70 g. of glycerol and about 1 cc. of concentrated sulphuric acid at 160-190°C., the reaction being considered complete when 3.5 parts of water have been distilled. The acidity of the resultant rubbery material is neutralized with sodium carbonate.

Aiken<sup>103</sup> reacted phenol and glycerol at 110°C. and added hydrogen chloride or, in some cases, concentrated hydrochloric acid to the mixture in order to take up the water formed during the reaction. Other substances such as anhydrous copper sulphate may be used to secure the same effect. The product is dehydrated and transformed to the infusible condition by heating with paraformaldehyde and ammonium carbonate. Glycerol may be replaced by other compounds, e.g., the glycols of ethylene, propylene, butylene or amylene. In place of ammonium carbonate in the second step, other catalysts suggested are sodium phenolate, calcium phenolate, sodium hydroxide, calcium oxide or potassium carbonate. In making a resin from phenol and polyhydric alcohols (e.g., glycerol) in the presence of a small quantity of sulphuric acid, Novotny and Romieux<sup>104</sup> provided means for removing the water from the zone of reaction as fast as it was formed.

Mixtures of phenols with glycerol and sulphonated fatty acids or naphtha sulphonic acids were heated at 120-140°C. in a process used by Petrov.<sup>105</sup> The viscous product is washed with water, neutralized with alkali, dehydrated and then heated with 40 per cent formaldehyde. The material is cooled, hydrochloric acid added and the mixture cast into molds and heated until sufficient hardness is obtained. Petrov and Schmidt<sup>106</sup> studied the formation of resins from phenols, glycerol and 4-12 per cent formaldehyde, using acid catalysts, e.g., sulphuric acid, sodium bisulphate and naphthene-sulphonic acids. The resins derived from phenol were reported to be free from phenolic odor. It was also stated that sodium bisulphate leads to a lighter colored resin, naphthene-sulphonic acids give a water-resisting product and that glycol cannot replace glycerol.

#### MISCELLANEOUS

Resins were made by Carter and Cox<sup>107</sup> by condensing an aliphatic dichloride, e.g., methylene dichloride, with a phenol in ammonium hydroxide solution. In this instance the chlorinated hydrocarbon and ammonia yield hexamethylenetetramine *in situ* which reacts with the phenol.<sup>108</sup> Thus, 5 cc. of phenol, 6.4 cc. of concentrated ammonium hydroxide and 2.4 cc. of methylene dichloride were heated in a closed vessel for 30 minutes at 180°C. The fusible soluble resins produced are kneaded with water to remove any ammonium chloride formed. The resin may be hardened with hexamethylenetetramine.

Solutions of ammonium chloride and hexamethylenetetramine obtained by heating methylene dichloride and ammonia together in aqueous solution can be boiled

<sup>102</sup> J. M. Coffey, U. S. P. 1,645,415, Oct. 11, 1927; *Chem. Abs.*, 1928, 22, 128. J. M. Coffey, British P. 288,260, 1928, to Mica Insulator Co.; *Brit. Chem. Abs.* B, 1929, 253.

<sup>103</sup> E. L. Aiken, U. S. P. 1,668,444 and 1,668,445, May 1, 1928, to Carboid Products Corp.; *Chem. Abs.*, 1928, 22, 2248.

<sup>104</sup> E. E. Novotny and C. J. Romieux, U. S. P. 1,705,494, Mar. 19, 1929, to J. S. Stokes; *Chem. Abs.*, 1929, 23, 2309.

<sup>105</sup> G. Petrov, German P. 407,002, 1922; *J.S.C.I.*, 1925, 44, 461B.

<sup>106</sup> G. Petrov and J. A. Schmidt, *Plast. Masses*, 1931, 1, 27; *Chem. Abs.*, 1932, 26, 3390.

<sup>107</sup> C. B. Carter and A. E. Cox, U. S. P. 1,543,369, June 23, 1925, to S. Karpen & Bros.; *Chem. Abs.*, 1925, 19, 2393. Canadian P. 234,506, 1923; *Chem. Abs.*, 1924, 18, 450. British P. 220,985, 1923; *Chem. Abs.*, 1925, 19, 902.

<sup>108</sup> For the preparation of hexamethylenetetramine from methylene dichloride, see C. B. Carter, U. S. P. 1,566,820, Dec. 22, 1925; *Chem. Abs.*, 1926, 20, 423, and also C. B. Carter and A. B. Cox, U. S. P. 1,499,001 and 1,499,002, June 24, 1924; *Chem. Abs.*, 1924, 18, 2524. British P. 246,415 and 246,416, 1925; *Chem. Abs.*, 1927, 21, 414. For the preparation of formaldehyde from methyl chloride see C. B. Carter and A. E. Cox, U. S. P. 1,459,971, June 26, 1923, to S. Karpen & Bros.; *Chem. Abs.*, 1923, 17, 2000.

under reflux with phenol to obtain a fusible resin.<sup>100</sup> A similar process has been described<sup>101</sup> in which the reaction is carried out in aqueous solution (under pressure) at 150-180°C. To obtain 4.6 kg. of a yellow resin sparingly soluble in alcohol and acetone, 4.8 kg. of methylene chloride, 6 kg. of phenol, 2 kg. of 24 per cent ammonium hydroxide and 26 kg. of water are heated together for 4-5 hours at 150-155°C. Sodium phenate was substituted by Prutton<sup>111</sup> for phenol in forming a condensation product with methylene dichloride. The resin obtained was a plastic gum when hot and a brittle solid when cold.

The preparation of fusible soluble resins from phenol and methylal,  $\text{CH}_3\text{OCH}_2\text{OCH}_3$ , is described by Carter and Coxe.<sup>112</sup> These are similar to the ones from phenol and formaldehyde, and are obtained by heating under pressure 3 mols of phenol with 2 mols of methylal for 1 hour at 180°C. using 0.05-0.1 per cent of hydrochloric acid as catalyst. The resins may likewise be rendered infusible by heating with hexamethylenetetramine or formaldehyde. The methylals can be made in satisfactory yield by heating sodium hydroxide, methylene chloride and the corresponding alcohol under pressure at 120°C. for 40 minutes.<sup>113</sup> Resins from phenol and methylal are obtained also by boiling the reactants under atmospheric pressure with 10-20 per cent of acid. One reaction mixture consists of 4.6 g. of methylal, 8.5 g. of phenol, 22.8 g. of water and 9.1 g. of sulphuric acid. Reaction is completed in the course of a few minutes.<sup>114</sup>

If solutions of paraform or trioxymethylene in mono- or polyhydric alcohols are heated with zinc oxide, alumina or aluminum hydroxide, a polymer of formaldehyde (melting at 98°C.) is obtained, according to Gebauer.<sup>115</sup> This product is a tallow-like solid, but liquefies at about 60°C. and is then miscible with most organic solvents. The use of solutions of the polymer for the production of phenol-formaldehyde resins has been suggested.

Considerable resinous matter was obtained by Huppmann<sup>116</sup> in the condensation of p-cresol methyl ether with p-benzoquinone. Similarly, allyl alcohol or an allyl ester and a phenol (e.g., o-cresol), using zinc chloride as catalyst, yield a resin said to be compatible with cellulose esters.<sup>117</sup>

Aliphatic or aromatic aldehydo-carboxylic<sup>118</sup> acids containing the carboxyl group either in the nucleus or the side chain may be condensed with phenols by the use of catalysts such as hydrochloric acid. For example, m-aldehydo-phenoxycetic acid may be melted with phenol and treated at 40-50°C. with concentrated hydrochloric acid. Stirring is continued until the mass is viscous. The acid is then washed out with hot water and the resulting soft product heated at 150°C. until a test portion solidifies to a hard resin.

In preparing  $\beta$ -resorcylaldehyde from diphenylformamidine and resorcinol at 100°C. and subsequent treatment with caustic soda solution, followed by acidification, Shoesmith and Haldane<sup>119</sup> found that a small amount of resin was also pre-

<sup>100</sup> C. B. Carter, U. S. P. 1,566,823, Dec. 22, 1925, to S. Karpen & Bros.; *Chem. Abs.*, 1926, 20, 484. British P. 255,692, 1925; *Chem. Abs.*, 1927, 21, 2932.

<sup>110</sup> British P. 196,265, 1923, to Holzverkohlungs-Ind. A.-G.; *Chem. Abs.*, 1923, 17, 3797.

<sup>111</sup> C. F. Prutton, U. S. P. 1,950,516, Mar. 13, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1934, 28, 3196.

<sup>112</sup> C. B. Carter and A. E. Coxe, U. S. P. 1,566,817, Dec. 22, 1925, to S. Karpen & Bros.; *Chem. Abs.*, 1926, 20, 484. Canadian P. 258,609, 1926; *Chem. Abs.*, 1926, 20, 3581. British P. 245,708, 1925; *Chem. Abs.*, 1927, 21, 307.

<sup>113</sup> C. B. Carter, U. S. P. 1,566,819, Dec. 22, 1925, to S. Karpen & Bros.; *Brit. Chem. Abs. B*, 1926, 217. British P. 249,039, 1925; *Chem. Abs.*, 1927, 21, 745.

<sup>114</sup> C. B. Carter, U. S. P. 1,645,226, Oct. 11, 1927; *Chem. Abs.*, 1927, 21, 4079.

<sup>115</sup> R. Gebauer, German P. 434,830, 1923, to Chem. Fabr. von Heyden A.-G.; *Brit. Chem. Abs. B*, 1927, 248.

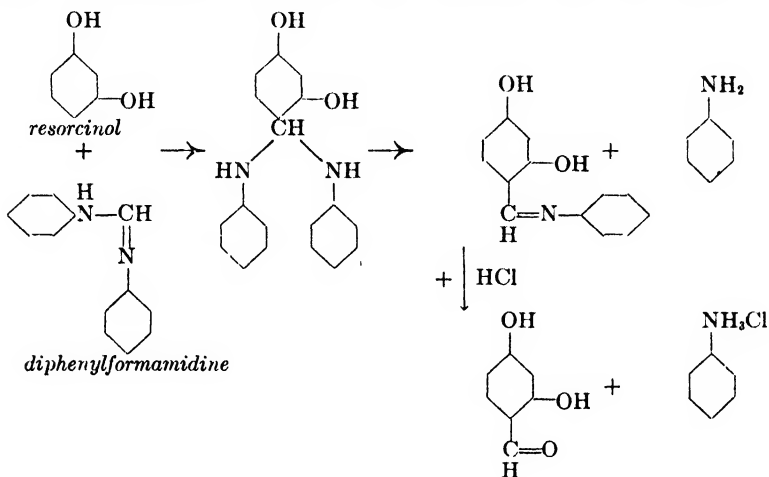
<sup>116</sup> G. Huppmann, *Süddeutsche Apoth.-Ztg.*, 1931, 71, 302; *Chem. Abs.*, 1931, 25, 3978.

<sup>117</sup> W. H. Moss and G. W. Seymour, U. S. P. 1,940,727, Dec. 26, 1933, to Celanese Co. of America; *Chem. Abs.*, 1934, 28, 1560. British P. 365,093 and 365,094, 1929; *Chem. Abs.*, 1933, 27, 1773.

<sup>118</sup> German P. 362,382, 1920, addn. to 339,495, to Farb. vorm. Meister, Lucius & Brining; *J.S.C.I.*, 1922, 41, 639A; 1923, 42, 613A.

<sup>119</sup> J. B. Shoesmith and J. Haldane, *J.C.S.*, 1923, 123 (2), 2704.

cipitated. This solidified on cooling and had a peculiar golden luster. Higher temperatures increased the degree of resinification and also caused formation of the dialdehyde of resorcinol. Maximum resin formation occurs at 200°C.



Resins were also formed in varying amounts when resorcinol was replaced by  $\alpha$ - and  $\beta$ -naphthol, guaiacol, pyrogallol and the cresols.<sup>120</sup>

<sup>120</sup> J. B. Shoemith and J. Haldane, *J.C.S.*, 1924, 125 (2), 2405.

## Chapter 19

# Modified Phenol-Aldehyde Resins

## I. Oil-Soluble Resins

It has already been stated (Chapter 2) that the demand of varnish manufacturers for more durable and quicker-drying finishes has resulted in the substitution of synthetic resins for natural resins formerly used. The durability and resistance of phenol resins led to attempts to employ them in oil varnishes. Difficulty was encountered at first, since phenol resins in the final stage are insoluble in drying oils.<sup>1</sup> Although the partly-cured resins (Novolaks) are soluble, their properties alter in time<sup>2</sup> and such resins lack the permanent quality possessed by those of the final stage. Hence investigations have been directed with a good measure of success to the incorporation of modifying agents to yield oil-soluble phenol resins which impart the desired durability to varnish films. The result has been the production of some phenol-resin varnishes which are quick-drying<sup>3</sup> and which furnish tough, flexible coatings sufficiently resistant to heat, moisture, sunlight and alkalis.<sup>4</sup>

### NATURAL RESIN MODIFIERS

The earliest method employed for making phenol-resins oil-soluble was to fuse them with a natural resin (rosin or copals). The resulting products possessed certain disadvantages which limited their application. For instance, they dissolved only after long heating, which prevented their use with the easily-polymerized tung oil; and once dissolved, they precipitated on dilution with hydrocarbon thinners. The earlier products darkened easily on exposure to light and apparently

<sup>1</sup> However finely ground resins dispersed in tung oil have been recommended (E. Elbel and F. Seebach, U. S. P. 1,880,930, Oct. 4, 1932, to Bakelite G m b.H.; *Chem. Abs.*, 1933, 27, 616. German P. 509,425, 1927; *Chem. Abs.*, 1931, 25, 833. German P. 519,469, 1928; *Chem. Abs.*, 1933, 27, 1217). F. Seebach, U. S. P. 1,816,128, July 28, 1931, to Bakelite G m b.H.; *Chem. Abs.*, 1931, 25, 5584. Cf. J. M. Taylor, U. S. P. 1,848,913, Mar. 8, 1932, to Continental-Diamond Fibre Co.; *Chem. Abs.*, 1932, 26, 2879.

<sup>2</sup> See C. T. O'Connor, *Am. Paint J. Conv. Daily*, 1934, 18 (53E), 10; *Brit. Chem. Abs. B*, 1935, 69.

<sup>3</sup> It has been reported that the speed of drying and the hardness of phenol-resin varnishes are proportional to the melting point of the resin. See *Circ., Natl. Paint, Varnish and Lacquer Assoc.*, 1934, 471, 319; *Chem. Abs.*, 1935, 29, 364.

<sup>4</sup> For reviews on this subject see H. Wolff, W. Toeldte and G. Zeidler, *Farben.-Ztg.*, 1928, 33, 1724; *Chem. Abs.*, 1928, 22, 3999. E. Fonrobert, *Farben.-Ztg.*, 1930, 35, 1506, 1554, 1608, 1658; *Chem. Abs.*, 1930, 24, 3356. E. E. Walker, *J.S.C.I.*, 1927, 46, 234. M. Bottler, *Kunststoffe*, 1927, 17, 149; *Chem. Abs.*, 1927, 21, 3137. A. W. C. Harrison, *Paint Manuf.*, 1932, 2, 243, 251; *Chem. Abs.*, 1933, 27, 199. H. Heberling, *Kunststoffe*, 1930, 20, 56; *Oberflächentechn.*, 1934, 11, 143; *Chem. Abs.*, 1934, 28, 5689. O. Nouvel, *Allgem. Öl Fett.-Ztg.*, 1931, 28, 188; *Chem. Abs.*, 1932, 26, 322. A. J. Norton, *Am. Paint J.*, 1931, 15 (30), 22 f.; *Chem. Abs.*, 1931, 25, 3501. H. M. Johnson, *Paint, Oil, Chem. Rev.*, 1932, 93 (22), 10; *Chem. Abs.*, 1932, 26, 4187. E. Fonrobert, *Kunststoffe*, 1922, 12, 121. D. H. Killeffer, *Sci. Am.*, 1931, 143, 238; *Chem. Abs.*, 1932, 26, 4966. F. G. Weed, *Paint, Oil, Chem. Rev.*, 1931, 91 (23), 12, 40; *Chem. Abs.*, 1931, 25, 3853. H. A. Gardner and G. G. Sward, *Circ., Am. Paint and Varnish Mfrs. Assoc.*, 1932, 410, 129; *Chem. Abs.*, 1932, 26, 3682. E. Fonrobert, *Synthetic and Applied Finishes*, 1935, 5, 249; *Chem. Abs.*, 1935, 29, 2003. *Paint, Oil, Chem. Rev.*, 1929, 88 (17), 89. H. Ulrich, *Farben.-Chem.*, 1935, 6, 12; *Brit. Chem. Abs. B*, 1935, 366.

were not true compounds, since rosin could be detected in many of them by the Storch-Morawski reaction.<sup>6</sup> These shortcomings were largely eliminated in the more modern products, in many of which rosin esters and polycumarone were used.<sup>6</sup>

In making a natural-resin-modified phenol resin Berend<sup>7</sup> observed that the fusion must be carried to a well-defined end-point in order to obtain a satisfactory material for oil varnishes. The end-point is reached when test specimens dropped on a glass plate remain clear in the cold, are soluble in fatty oils, and do not precipitate from solution on the addition of benzene or turpentine. It was found that a 3-hour heating at 300°C. was necessary to accomplish this result.<sup>8</sup> The suggestion has been made that some rosin-modified phenol resins are improved if the volatile constituents of the natural resin are removed by distillation.<sup>9</sup> Thus, Spanish rosin is fused at 150°C. with cresol-formaldehyde resin and the mixture is heated at 250°C. for 200 hours. The resulting mass is distilled *in vacuo* to give a clear substance (m. p. 110-120°C.) with an acid number of 42.

Berend<sup>10</sup> transformed infusible, insoluble phenol-aldehyde resins to soluble, fusible materials by heating them with polycumarone or rosin. This principle has been utilized to convert molding scrap into varnish material.<sup>11</sup> The synthetic resin is heated with colophony to give a product soluble in benzene, turpentine and linseed oil.

Champetier and Laporte,<sup>12</sup> in order to determine the exact effect of the fusion of a phenol resin with colophony, carried out the process in various ways. Phenol was condensed with formalin in the presence of hydrochloric acid, the reaction being stopped at the moment of turbidity. The resin which was obtained was mixed with colophony and heated at approximately 300°C. in a carbon dioxide atmosphere or in an autoclave. These two methods were varied by refluxing the mixture initially, by heating the rosin first at 90°C., or by distilling the product after fusion. It was found that free phenol is susceptible to esterification with abietic acid under these conditions, and that the rate of reaction increases rapidly as the temperature is raised above 285°C. Resin ester in the product increases the solubility in oil but lowers the fusion point. Also the solubility is improved by increase in the proportion of rosin but is decreased by the acids catalyzing the condensation or esterification. Prolonged heating at elevated temperatures decreases the acid number and raises the fusion temperature.

Pistor<sup>13</sup> found that an acid interchange took place when fatty acid glycerides were heated with either natural or oil-soluble synthetic resins. He considers that a distinct advantage is derived by the employment of neutral Albertol resins, since only a small amount of fatty acid is liberated as compared with the quantity yielded by copal or colophony.

<sup>6</sup> See E. Elsner, *Farben-Ztg.*, 1928, 33, 2547. M. Schulz, *ibid.*, 2741.

<sup>7</sup> L. Berend, *Z. angew. Chem.*, 1923, 36, 242; *Chem. Abs.*, 1923, 17, 2789. A. Eibner, *Z. angew. Chem.*, 1923, 36, 33; *Chem. Abs.*, 1923, 17, 3796. E. Fonrobert, *Kunststoffe*, 1923, 13, 109; *Chem. Age*, (N.Y.), 1924, 32, 167, 221, *Chem. Abs.*, 1924, 18, 2611.

<sup>8</sup> L. Berend, U. S. P. 1,205,081, Nov. 14, 1916; *Chem. Abs.*, 1917, 11, 216. British P. 15,875, 1914; *J.S.C.I.*, 1915, 34, 805. Swiss P. 72,631, 1916; *Chem. Abs.*, 1916, 10, 2646. German P. 289,968, 1914, addn to 281,939.

<sup>9</sup> E. H. Fayolle (French P. 341,013, 1904; *J.S.C.I.*, 1904, 23, 873) noted that a rubber-like substance is obtained by heating phenol resin (1 part) with rosin (2 parts).

<sup>10</sup> German P. 548,656, 1924, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1932, 26, 4191.

<sup>11</sup> L. Berend, U. S. P. 1,259,347, Mar. 12, 1918; *Chem. Abs.*, 1918, 12, 1517. British P. 107,205, 1916; *Chem. Abs.*, 1917, 11, 3396. Swedish P. 40,460, 1916. See also H. Gammay, British P. 386,179, 1932, to Chemicon A.-G.; *Brit. Chem. Abs.*, B, 1933, 238. German P. 554,490, 1929, to K. Albert G.m.b.H.; *Chem. Abs.*, 1932, 26, 5221. A. Voss, German P. 374,379, 1920, and 376,729, 1921, to Farb. vorm. Meister, Lucius & Brünning; *J.S.C.I.*, 1923, 42, 1141A. T. Syôno, Japanese P. 101,618, 1933; *Chem. Abs.*, 1934, 28, 5263. Japanese P. 99,551, 1933; *Chem. Abs.*, 1934, 28, 2487. K. Iwamura and T. Hattori, Japanese P. 90,904, 1931; *Chem. Abs.*, 1931, 25, 5050.

<sup>12</sup> H. Bucherer, German P. 456,820, 1924, addn. to 391,072, 1912; *Chem. Zentr.*, 1928, 1, 3002.

<sup>13</sup> Champetier and Laporte, *Recherches et inventions*, 1934, 15, 230, 252, 291; *Chem. Abs.*, 1935, 29, 249.

<sup>14</sup> K. Pistor, *Farben-Ztg.*, 1925, 30, 3056; *J.S.C.I.*, 1925, 44, 930.

It has been stated by Dupont and Man-Tcheung<sup>14</sup> that in making a rosin-modified phenol resin the best results are obtained by employing a condensation product from equimolecular proportions of phenol and formaldehyde (catalyzed with 1 per cent hydrochloric acid). Thirty parts of this resin are fused with 70 parts of rosin at 120-130°C., then 0.4 per cent of calcium oxide is added and the temperature is raised and maintained at 290°C. until the product is completely oil-soluble.

Oil-soluble resins for varnishes have been obtained by fusing the condensation product of salicylic acid and formaldehyde with rosin. The original object of this procedure was to raise the melting point of rosin and not to obtain a modified phenol resin.<sup>15</sup> Other modified resins include phenol-aldehyde condensation products fused with benzoic, salicylic, palmitic or oleic acid<sup>16</sup> and mixed phenol-aldehyde-alkyd resins fused with colophony.<sup>17</sup>

In addition to fusing natural resins with phenol-aldehyde condensation products, attempts were also made to incorporate the natural resin directly in the initial condensation. Albert and Berend<sup>18</sup> reacted phenol and formaldehyde in the presence of 5 per cent of natural resins, which act as catalysts. Some of the resinous bodies thus formed were oil-soluble and could be saponified.<sup>19</sup> Later it was discovered that only when the rosin, balsams, or similar materials were used in quantities greater than required for their action as catalysts would the product be soluble in oil.<sup>20</sup> The process allows any free phenol remaining to be combined with formaldehyde which may be added later. A mixture of 100 grams of phenol, 100 grams of rosin, and 30 grams of trioxymethylene is heated under reflux at 115-120°C. for 6 hours. The temperature is then raised to 200°C. and the reaction mass stirred to remove volatile constituents.<sup>21</sup> A more soluble material is obtained when 95 g. of phenol, 70 g. of 40 per cent formaldehyde, and 2 g. of hydrochloric acid are heated for 6 hours with 30 g. of Manila copal. The use of a basic catalyst has also been suggested in this procedure,<sup>22</sup> but prolonged heating yields an insoluble substance. The procedure has been further modified by heating the resin or resin acid of copaiba balsam with phenol, and then adding formaldehyde and hydrochloric acid.<sup>23</sup>

Promising results were obtained with a phenol-formaldehyde-colophony condensation product in coatings for the protection of ship-bottoms from marine growths. The effect may be due to the presence of free formaldehyde or phenol bodies, which have a toxic influence.<sup>24</sup>

Japanese lac has been proposed as a modifier.<sup>25</sup> An intimate mixture of 100 parts of phenol, 200 parts of formalin and 50 parts of Japanese lac were heated

<sup>14</sup> G. Dupont and L. Man-Tcheung, *Bull. inst. pin.*, 1934, 89; *Chem. Abs.*, 1934, 28, 6000

<sup>15</sup> A. Voss, German P. 422,910, 1921, to Farb- u. vorm. Meister, Lucius & Brüning; *Brit. Chem. Abs.*, 1926, 502.

<sup>16</sup> R. Hessen, British P. 206,469, 1923, addn. to 159,461, to Bakelite G.m.b.H.; *Chem. Abs.*, 1924, 18, 1210. German P. 410,858, 1922, addn. to 340,990; *Kunststoffe*, 1925, 15, 182.

<sup>17</sup> W. J. R. Evans and R. Hill, British P. 367,001, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.*, 1932, 437. French P. 731,240, 1932; *Chem. Abs.*, 1933, 27, 858.

<sup>18</sup> K. Albert and L. Berend, British P. 1269, 1912; *J.S.C.I.*, 1913, 32, 35. French P. 441,547, 1912; *J.S.C.I.*, 1912, 31, 886. German P. 254,411, 1910; *Chem. Abs.*, 1913, 7, 1299. German P. 269,659, 1911; *Chem. Abs.*, 1914, 8, 2269.

<sup>19</sup> Aqueous solutions for coating and impregnating paper have been made from phenol resins containing small amounts of rosin. Phenol (1 part), formaldehyde (0.9 part), and sodium hydroxide (0.03 part) are boiled together in aqueous solution for 30 minutes. Powdered rosin (0.38 part) and hexamethylenetetramine (0.09 part) are added, and the mixture is cooled. L. M. Rossi, U. S. P. 1,813,724, Jan. 11, 1927, to Bakelite Corp.; *Chem. Abs.*, 1927, 21, 828.

<sup>20</sup> L. Berend, U. S. P. 1,191,390, July 18, 1916; *Chem. Abs.*, 1916, 10, 2208. German P. 281,939, 1913; *J.S.C.I.*, 1915, 34, 724.

<sup>21</sup> Aldol or crotonaldehyde may be substituted for the formaldehyde. See G. Balle and H. Wohlers, German P. 406,153, 1922, to Farb- u. vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1925, 44, 461B.

<sup>22</sup> I. S. Mellanoff, U. S. P. 1,804,379, May 5, 1931, to Kemikal, Inc.; *Chem. Abs.*, 1931, 25, 3782.

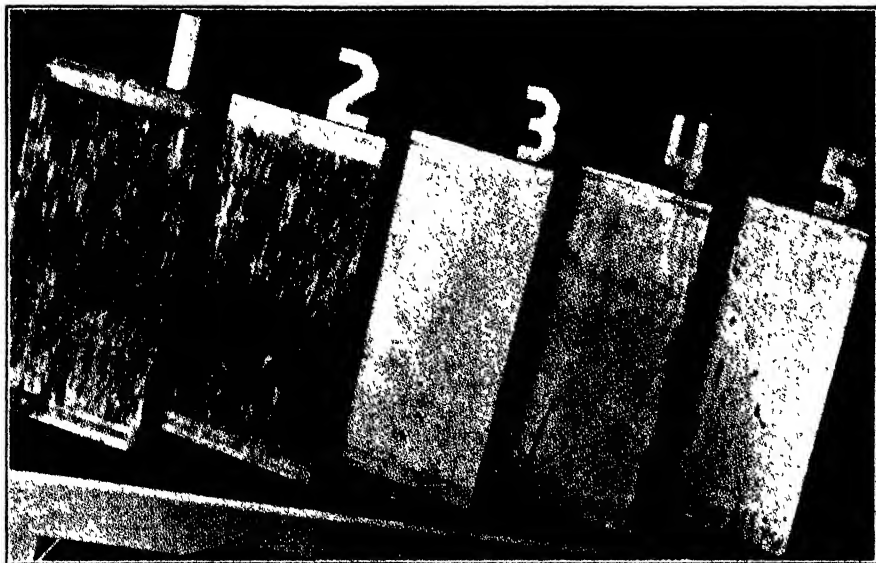
<sup>23</sup> K. A. Lingner, French P. 886,002, 1908; *Chem. Abs.*, 1909, 3, 2860.

<sup>24</sup> H. A. Gardner, *Circ.*, U. S. Paint Mfrs. Assoc., 1926, 259, 232; *Chem. Abs.*, 1926, 20, 1329.

<sup>25</sup> K. Hatta and K. Nakajima, Japanese P. 39,310, 1921, to Nippon Kwako K. K.; *Chem. Abs.*, 1922, 16, 2787.

for 48 hours at 120°C. The residue, after distillation and separation of the excess formaldehyde, is an oil-soluble resin.

After incorporation of rosin, phenol-formaldehyde resins may be esterified with glycerol.<sup>26</sup> The product obtained is more soluble in drying oils, has a greater molecular weight, and yields solutions of greater viscosity. Compared with ester gum, it possesses more resistance to alkali and weathering influences. The preparation is as follows: 100 parts of cresol are heated with 400 parts of rosin and 40 parts of paraformaldehyde until the cresol has entirely disappeared and a tough resinous mass which remains clear in the cold is produced. The resin is dehydrated



Courtesy General Plastics, Inc.

FIG. 67.—Varnishes Exposed for Two Months to Sub-Tropical Conditions. Panels 3, 4 and 5 are coated with Durez varnishes.

by heating at 250°C. and 50 parts of glycerol are gradually added. Heating is continued for several hours to complete the reaction. A phenolic condensation product containing a reactive hydroxymethyl group (p-cresol-dialcohol, 10 parts)<sup>27</sup> may be heated with rosin (100 parts) and finally esterified to give an oil-soluble resin.<sup>28</sup> Phenol-alcohols may also be esterified by such acids as oleic, palmitic, abietic, phthalic, phosphoric<sup>29</sup> or pyroabietic.<sup>30</sup>

A resin resulting from the heating of phenol, formaldehyde, and colophony may be modified by treatment with the monoesters or monoethers of glycol,<sup>31</sup> with butyl

<sup>26</sup> A. Amann and E. Fonrobert, U. S. P. 1,623,901, Apr. 5, 1927, to Chem. Fabr. K. Albert G. m. b. H.; *Chem. Abs.*, 1927, 21, 1717. British P. 259,030, 1925; *Chem. Abs.*, 1927, 21, 3276. German P. 440,003, 1917; *Brit. Chem. Abs. B*, 1929, 27. See also German P. 480,488, 1921, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1929, 23, 5051. German P. 492,592, 1924, addn. to 440,003, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1930, 24, 2623.

<sup>27</sup> For the preparation of phenol-alcohols see Chapter 14.

<sup>28</sup> A. Amann, U. S. P. 1,736,757, Nov. 19, 1929, to Chem. Fabr. K. Albert G. m. b. H.; *Chem. Abs.*, 1930, 24, 740. German P. 474,737, 1923, addn. to 440,003; *Chem. Abs.*, 1929, 23, 3114.

<sup>29</sup> German P. 474,561, 1925, to Chem. Fabr. K. Albert G.m.b.H.; see also French P. 526,968.

<sup>30</sup> Austrian P. 117,856, 1930, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Zentr.*, 1930, 2, 1291. See also H. Hönel, German P. 601,262, 1934; *Chem. Abs.*, 1934, 28, 7564.

<sup>31</sup> German P. 509,388, 1928, to Chem. Fabr. K. Albert G. m. b. H.; *Chem. Abs.*, 1931, 25, 710.

phthalate or benzyl acetate,<sup>32</sup> or with a metallic soap or rosin or of a fatty acid.<sup>33</sup>

Rosenblum<sup>34</sup> employed resin esters to modify phenol-aldehyde resins. His method is as follows: 100 parts of cresol, dissolved in 100 parts of turpentine, are heated at 100°C. with 100 parts of 40 per cent formaldehyde until reaction is complete. After separation of water by distillation, 100 parts of the resulting solution are heated with 120 parts of a mixture of 25 per cent glyceryl diacetate and 75 per cent glyceryl triacetate.<sup>35</sup> The resin, after removal of volatile constituents by distillation, has an acid number of 10 or less. A variation of the procedure includes the addition of the resinates or oleates of zinc, calcium or barium.<sup>36</sup> Cracked rosin may be substituted for the ordinary rosin.<sup>37</sup> In another instance, the condensate from p-phenyl phenol, zinc acetate and formaldehyde is heated with rosin ester gum.<sup>38</sup>

A resin-ester-modified phenol resin was made by Binapfl<sup>39</sup> by condensing colophony with crude cresol in the presence of boron fluoride, esterifying the product with glycerol and then treating with paraformaldehyde. Natural resin esters may be hardened by treatment with synthetic resins.<sup>40</sup> For example, 100 parts of phenol-dialcohol and 100 parts of paraldehyde-phenol condensation product are melted together, and 800 parts of rosin-glycerol ester are added. The mass is heated for several hours, first at 150°C. and then at 250°C. Heating is continued until the melting point is constant. The product formed has its melting point raised from 68° to 100°C. and is soluble in linseed oil.

Neutral resin esters are prepared by esterifying a mixture of natural or synthetic resin acids and compounds containing the hydroxyl group, the resin acid and hydroxyl-containing substances being present in equivalent proportions.<sup>41</sup> For example, a phenol-aldehyde resin is melted in glycerol and rosin is added. The reaction is catalyzed with boric acid. Similarly the condensation product of cresol hydroxymethyl ether and formaldehyde heated at 200-250°C. with rosin gives a resin with a low acid number.<sup>42</sup>

A resinous mixture for lacquers was obtained by Bielouss<sup>43</sup> by esterifying a phenol-formaldehyde-rosin condensation product with glycerol and then forming in the resultant mass a second synthetic resin from glycerol and phthalic anhydride.<sup>44</sup> In a process employed by Balle,<sup>45</sup> a rosin-modified phenol resin containing

<sup>32</sup> British P. 353,616, 1930, to Chem. Fabr. K. Albert G. m. b. H., *Brit. Chem. Abs.*, B, 1931, 1019.

<sup>33</sup> R. E. Coleman, British P. 411,744, 1934, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1934, 28, 7043.

<sup>34</sup> I. Rosenblum, U. S. P. 1,709,490, Apr. 16, 1929, to Varnol Chem. Corp.; *Chem. Abs.*, 1929, 23, 2842. U. S. P. 1,928,507, Aug. 22, 1933; *Chem. Abs.*, 1933, 27, 5203. British P. 315,870, 1929, *Brit. Chem. Abs.*, B, 1931, 170. See also S. Sugimoto, *Repts. Imp. Ind. Research Inst.*, Osaka, Japan, 1933, 14 (13), 1; *Chem. Abs.*, 1934, 28, 4921.

<sup>35</sup> For a discussion of ester gum, see Chapter 38.

<sup>36</sup> I. Rosenblum, U. S. P. 1,808,716, June 2, 1931, to Varnol Chem. Corp.; *Chem. Abs.*, 1931, 25, 4422. French P. 704,116, 1930; *Chem. Abs.*, 1931, 25, 4726. British P. 370,916 and 370,946, 1930, *Brit. Chem. Abs.*, B, 1932, 808.

<sup>37</sup> I. Rosenblum, U. S. P. 1,809,570, June 9, 1931, to Varnol Chem. Corp., *Brit. Chem. Abs.*, B, 1932, 119. British P. 371,850, 1930; *Brit. Chem. Abs.*, B, 1932, 563. French P. 705,091, 1930; *Chem. Abs.*, 1931, 25, 5305.

<sup>38</sup> I. Rosenblum, British P. 406,652, 1934; *Chem. Abs.*, 1934, 28, 4924.

<sup>39</sup> J. Binapfl, German P. 532,847, 1933 and 605,688, 1934, addns. to 581,956, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 919; 1935, 29, 1906. German P. 532,848, 1933; *Chem. Abs.*, 1934, 28, 920.

<sup>40</sup> E. Asser, U. S. P. 1,969,292, Aug. 7, 1934; *Chem. Abs.*, 1934, 28, 6329. British P. 404,060, 1934; *Chem. Abs.*, 1934, 28, 3922. French P. 740,030, 1932; *Chem. Abs.*, 1933, 27, 2320. German P. 565,800, 1930; *Chem. Abs.*, 1933, 27, 3095.

<sup>41</sup> G. Balle and A. Voss, German P. 521,727, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3503.

<sup>42</sup> G. Balle, German P. 604,459, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 854.

<sup>43</sup> E. Bielouss, U. S. P. 1,866,962, July 12, 1932, to H. A. Gardner Lab. Inc.; *Chem. Abs.*, 1932, 26, 4726.

<sup>44</sup> See also Chapter 45.

<sup>45</sup> G. Balle, German P. 510,446, 1928, addn. to 463,842, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1109.



excess resin acid is treated with acetylene in the presence of mercuric sulphate to yield a hard resin soluble in hydrocarbons.

For the preparation of varnishes, tung oil may be heated with boric or oxalic acid, which allows polymerization but retards gelatinization. The treated oil is then incorporated with an oil-soluble phenolic resin to give a coating composition.<sup>44</sup>

The reaction between drying oils and oil-soluble resins, at least in the case of Amberols and tung oil, is considered to be one of chemical combination.<sup>45</sup> Mixed esters are apparently formed and the varnish film can be regarded as a synthetic resin. Viscosity measurements during cooking of tung-oil-resin varnishes indicate that chemical polymerization (or condensation) first occurs, followed by physical aggregation or gel formation.<sup>46</sup>

One form of Albertol resin has been used for testing tung oil varnishes. The "Albertol number"<sup>47</sup> is defined as the per cent by weight of Albertol 111 L that must be added (as 50 per cent solution in benzene) to tung oil (containing 0.1 per cent of cobalt as resinate), to yield a non-frosting film when dried in an oven (English Standard Specification 256). Brendel suggested use of other resins in this test and recommended that the term "frosting number" be used.<sup>48</sup>

After investigations as to the effect of driers on Amberol-linseed oil varnishes, Sward and Gardner<sup>49</sup> made the following generalizations: Fastest drying was obtained by the addition of 0.5 per cent lead linoleate and 0.2 per cent manganese linoleate. Large amounts of driers tend to produce brittleness and do not accelerate drying. Manganese driers reduce the elasticity of the films and induce skinning on storage to a greater extent than the lead or cobalt compounds.

Although most of the oil-soluble resins are used in the making of varnishes,<sup>50</sup> they may also be employed in the manufacture of linoleum,<sup>51</sup> printing inks,<sup>52</sup> imitation leather finish,<sup>53</sup> adhesives,<sup>54</sup> transfer and marking compositions,<sup>55</sup> coatings for cans,<sup>56</sup> coatings for paper,<sup>57</sup> and plastic mixtures for insulation.<sup>58</sup> An aluminum salt

<sup>44</sup> R. E. Coleman, British P. 413,162, 1934, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1935, 29, 628.

<sup>45</sup> R. L. Houck, *Paint, Oil, Chem. Rev.*, 1928, 86 (21), 10; *Chem. Abs.*, 1929, 23, 5836.

<sup>46</sup> V. H. Turkington, R. C. Shuey and W. H. Butler, *Ind. Eng. Chem.*, 1931, 23, 791. See also H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," Institute of Paint and Varnish Research, Washington, D. C., 1927, 436.

<sup>47</sup> E. Fonrobert and C. Boller, *Farben-Ztg.*, 1931, 36, 2196, 2239; 37, 15; *Chem. Abs.*, 1932, 26, 322; *Brit. Chem. Abs. B*, 1931, 1060.

<sup>48</sup> H. Brendel, *Farbe u. Lack*, 1932, 145; *Brit. Chem. Abs. B*, 1932, 612.

<sup>49</sup> G. Sward and H. A. Gardner, *Circ., Am. Paint and Varnish Mfrs. Assoc.*, 1927, 301, 135; *Chem. Abs.*, 1927, 21, 1191.

<sup>50</sup> T. H. Barry, *Ind. Chemist*, 1928, 4, 501, 1930, 6, 69; *Chem. Abs.*, 1929, 23, 1292; 1930, 24, 2315. E. Eibner and U. Munzert, *Farben-Ztg.*, 1924, 29, 1847; *Chem. Abs.*, 1925, 19, 408. E. Fonrobert, *Farben-Ztg.*, 1934, 39, 548, 577; *Brit. Chem. Abs. B*, 1934, 637; *Kunststoffe*, 1931, 24, 145, 178; *Chem. Abs.*, 1931, 25, 5583. E. Fonrobert, C. P. Holdt and F. Wilborn, *Farben-Ztg.*, 1934, 39, 89, 113; *Chem. Abs.*, 1934, 28, 2925. J. H. Frydender, *Rev. prod. chim.*, 1928, 31, 661; *Chem. Abs.*, 1929, 23, 531. H. A. Gardner, *Circ. Am. Paint, Varnish Mfrs. Assoc.*, 1926, 261, 275; 1928, 323; *Chem. Abs.*, 1926, 20, 2756. H. A. Gardner and J. B. Faust, *ibid.*, 1926, 277, 83; *Chem. Abs.*, 1926, 20, 3354. E. J. Probeck, *Paint, Oil, Chem. Rev.*, 1928, 86 (17), 108. A. E. Stauderman, *Circ. Am. Paint, Varnish Mfrs. Assoc.*, 1929, 356, 815; *Paint, Oil, Chem. Rev.*, 1929, 86 (17), 89; *Chem. Abs.*, 1930, 24, 514. A. E. Stauderman and H. L. Beakes, *Ind. Eng. Chem.*, 1928, 20, 674. H. Wolff and G. Zeidler, *Farben-Ztg.*, 1929, 34, 2458; *Chem. Abs.*, 1929, 23, 4834. *Decorator*, 1934, 32 (336), 28; *Brit. Chem. Abs. B*, 1934, 771. K. Buser, *Farbe u. Lack*, 1935, 63; *Chem. Abs.*, 1935, 29, 3180. *Seifensieder-Ztg.*, 1930, 57, 765. Arnold, *Chem.-Ztg.*, 1932, 56, 55; *Chem. Abs.*, 1932, 26, 2806. A. Herrmann, *Gelatine, Leim, Klebstoffe*, 1934, 2, 249; *Chem. Abs.*, 1935, 29, 1663. G. Dring, *J. Oil, Colour Chem. Assoc.*, 1934, 17, 459; *Chem. Abs.*, 1935, 29, 1665. E. Stock, *Kunststoffe*, 1927, 17, 77; *Chem. Abs.*, 1927, 21, 3136.

<sup>51</sup> I. M. Finghaus and V. M. Breitman, *Plast. Masses*, 1933 (5), 14; *Chimie et industrie*, 1933, 31, 1417; *Chem. Abs.*, 1934, 28, 6000.

<sup>52</sup> British P. 408,688, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 6001. E. Fonrobert, *Am. Ink Maker*, 1931, 9 (12), 17, 33; 1932, 10 (1), 19; *Chem. Abs.*, 1932, 26, 1806; *Farben-Ztg.*, 1930-31, 36, 265, 1383; *Brit. Chem. Abs. B*, 1931, 642. W. Lutzendorf, German P. 585,167, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1556.

<sup>53</sup> D. M. Philippi, U. S. P. 1,936,913, Nov. 28, 1933, to Kay & Ess Chem. Corp.; *Brit. Chem. Abs. B*, 1934, 849.

<sup>54</sup> British P. 347,445, 1930, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B*, 1931, 637.

<sup>55</sup> W. S. Lawrence, U. S. P. 1,977,680, Oct. 23, 1934, to Kaumagraph Co.; *Chem. Abs.*, 1935, 29, 258. U. S. P. 1,954,450 and 1,954,451, Apr. 10, 1934; *Brit. Chem. Abs. B*, 1935, 110.

<sup>56</sup> G. Terajima, Japanese P. 101,159, 1933, to Hokkai Seikan Soko K. K.; *Chem. Abs.*, 1934, 28, 5263.

<sup>57</sup> French P. 740,212, 1931, to Compagnie des vernis Valentine; *Chem. Abs.*, 1933, 27, 2301.

<sup>58</sup> H. A. Tunstall and F. G. Richard, British P. 409,672, 1932, to W. T. Henleys Telegraph Works Co.; *Brit. Chem. Abs. B*, 1934, 592.

of a high-acid Albertol resin has been investigated and suggested as a flattening-medium for varnishes.<sup>61</sup> A short-oil Albertol-tung oil varnish has been recommended as a water-resistant priming coat.<sup>62</sup> Another varnish which has been suggested is made by melting an Amberol resin with  $\beta$ -eleostearin at 210°C.; lead oxide and manganese dioxide are added and the temperature raised to 275°C. High-boiling gasoline is used as the solvent.<sup>63</sup>

The use of Albertol resins in nitrocellulose lacquers is recommended because of their neutrality, purity and uniformity, as well as the conferment of increased alkali resistance. They are soluble for the most part in solvents for such lacquers (acetone, amyl or ethyl acetate, Cellosolve, xylene or turpentine). Combination lacquers (oil and nitrocellulose) present another field of use. Because the Albertols (Amberols) are hard resins, a plasticizer is advisable.<sup>64</sup>

### OIL-MODIFIED PHENOL RESINS

In the search for oil-soluble phenol resins it was observed that the desired properties are obtained not only by incorporation of natural resins but also by the use of drying oils as modifiers. Tung oil is the most widely employed oil for this purpose.

One method of producing an oil-modified phenol resin is described by Brown.<sup>65</sup> Twelve parts of raw tung oil and 15 parts of a lead and manganese-tungate and-resinate drier are heated in an open kettle to 180-190°C. as rapidly as possible and maintained at that temperature for about 15 minutes. The liquid is allowed to cool to 100°C. and 4 parts of cresol and 3 parts of 40 per cent formaldehyde solution are added. The temperature of the mixture is maintained at 95-100°C. for 1 hour with stirring, this treatment effecting evaporation of most of the water. Heating is then stopped and the mixture is permitted to stand for several hours. Precipitated sediment is removed and the temperature is raised to nearly 150°C. until the odor of formaldehyde has disappeared. The material is thinned with kerosene or turpentine to form a baking varnish. The use of a smaller proportion of tung oil results in the formation of a product which may be used for the impregnation of cloth and fiber.<sup>66</sup> The procedure may be altered by heating the tung oil and phenol together, adding later the aldehyde and drier.<sup>67</sup> By varying the proportions and omitting the drier, a plastic composition for insulation is obtained.<sup>68</sup>

The reaction of oxidation products of linseed oil or of tung oil with phenol and formaldehyde, employing a basic catalyst such as ammonia, yields a resin which is said to be resistant to acids.<sup>69</sup> It is soluble in toluene and xylene and may be used in the insulation of electrical apparatus.<sup>70</sup> The product obtained by the interaction of 100 parts of cresol, 100 parts of tung oil, and 20 parts of hexamethylenetetramine is soluble in turpentine, and with driers forms a resistant film at room temperature.<sup>71</sup> Combination of phenol, or cresol, formaldehyde

<sup>61</sup> E. Fonrobert, *Farben-Ztg.*, 1932, 37, 1084; *Chem. Abs.*, 1932, 26, 3682. H. Wolff and B. Rosen, *Farben-Ztg.*, 1933, 38, 704; *Chem. Abs.*, 1933, 27, 2828.

<sup>62</sup> H. Wolff and G. Zeidler, *Farben-Ztg.*, 1934, 39, 1071; *Brit. Chem. Abs. B*, 1934, 1069. See also A. V. Blom, *Verkronek*, 1934, 7, 279; *Chem. Abs.*, 1935, 29, 2001.

<sup>63</sup> C. G. Gauerke, British P. 312,052, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 24, 980.

<sup>64</sup> A. Kraus, *Farbe u. Lack*, 1930, 206, 221, 586; *Chem. Abs.*, 1930, 24, 4174.

<sup>65</sup> A. L. Brown, U. S. P. 1,212,733, Jan. 16, 1917, to Westinghouse Elec. & Mfg. Co.; *J.S.C.I.*, 1917, 36, 396.

<sup>66</sup> A. L. Brown, U. S. P. 1,632,113, June 14, 1927, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1927, 21, 2539. U. S. P. 1,633,976, June 28, 1927; *Chem. Abs.*, 1927, 21, 2764. U. S. P. 1,820,690, Aug. 25, 1931; *Chem. Abs.*, 1931, 25, 5740. Canadian P. 261,122, 1926; *Chem. Abs.*, 1926, 20, 2567.

<sup>67</sup> A. L. Brown, U. S. P. 1,640,562, Aug. 30, 1927, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1927, 21, 3473.

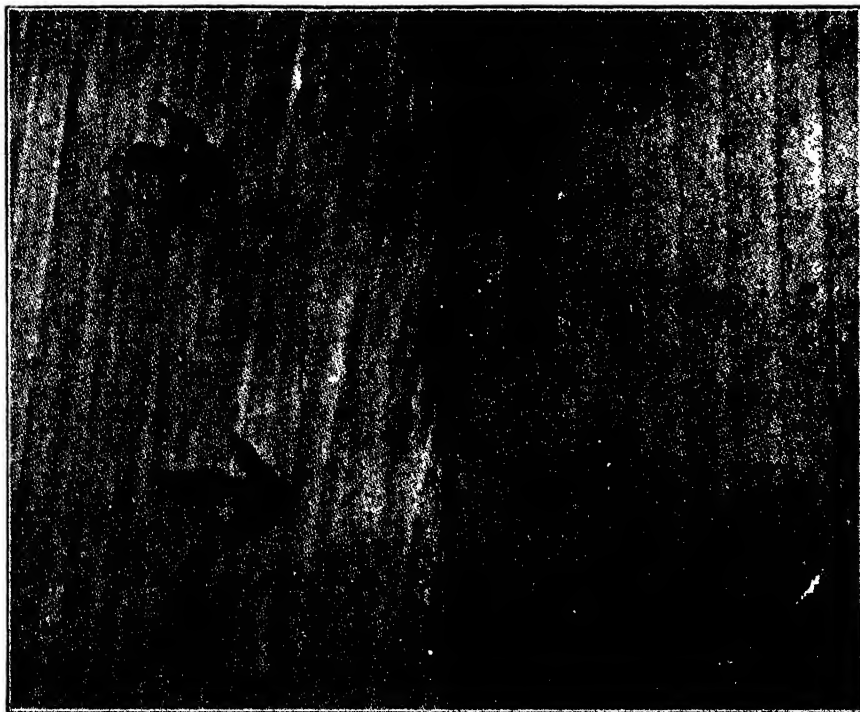
<sup>68</sup> A. L. Brown, U. S. P. 1,680,403, Aug. 14, 1928, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1928, 22, 3792.

<sup>69</sup> K. Bickhardt, German P. 534,784, 1926; *Chem. Abs.*, 1932, 26, 1143.

<sup>70</sup> A. Heck, U. S. P. 1,947,414 and 1,947,415, Feb. 13, 1934, to Cook Paint & Varnish Co.; *Chem. Abs.*, 1934, 28, 2554. Canadian P. 329,051, 1933; *Chem. Abs.*, 1933, 27, 1530.

<sup>71</sup> V. Turkington, British P. 349,522, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 728. French P. 690,763, 1930; *Chem. Abs.*, 1931, 25, 1692. Canadian P. 308,848, 1931; *Chem. Abs.*, 1931, 25, 2012.

and tung oil is effected by heating the mixture at 100-150°C. A catalyst is not necessary, but use of a closed vessel enables the reaction to be carried out under pressure. Bodied tung oil may replace the raw oil. Dehydration is accomplished by subjecting the condensate to a vacuum at 100°C. or less. Varnishes made by this method give coatings which, after baking, are reported to have exceptional toughness, flexibility and dielectric strength.<sup>72</sup> Similarly, the reaction of xylolol



Courtesy General Plastics, Inc.

FIG. 68.—House-Paint Weathering Test. On the left, straight oil and white lead formulation. On the right, paint fortified with Durez resin.

with paraformaldehyde in tung oil in the presence of triethanolamine as a catalyst yields a substance which may be dissolved in naphtha.<sup>73</sup>

An oil-modified resin described by Croad<sup>74</sup> is prepared by condensing 2 mols of a phenol (e.g., cresylic acid) with 1 mol of formaldehyde in a solution (e.g., sodium acetate) which is only slightly alkaline to alizarin-red S and then heating the product with tung or linseed oil.

Byck<sup>75</sup> has made a coating composition by boiling 100 parts of phenol, 150

<sup>72</sup> N. Strafford, U. S. P. 1,928,739, Oct. 3, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 5995. British P. 350,896, 1930; *Brit. Chem. Abs. B.*, 1931, 818.

<sup>73</sup> C. S. Ferguson, U. S. P. 1,896,842, Feb. 7, 1933, to Gen. Elec. Co.; *Chem. Abs.*, 1933, 27, 2831. Canadian P. 342,585, 1934, to Can. Gen. Elec. Co.; *Chem. Abs.*, 1934, 28, 6002. See also G. H. Mains, U. S. P. 1,730,857, Oct. 8, 1929, to Westinghouse Elec. & Mfg. Co.; *Brit. Chem. Abs. B.*, 1929, 987.

<sup>74</sup> R. B. Croad, British P. 411,828, 1934, to Howroyd, McArthur & Co., Ltd.; *Chem. Abs.*, 1934, 28, 7044.

<sup>75</sup> L. C. Byck, U. S. P. 1,887,833, Nov. 15, 1932, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 1464. U. S. P. 1,590,079, June 22, 1926; *Chem. Abs.*, 1926, 20, 3090. British P. 267,738, 1926; *Chem. Abs.*, 1928, 22, 1245. German P. 504,682, 1926; *Chem. Abs.*, 1931, 25, 425. German P. 497,790, 1926; *Chem. Abs.*,

parts of tung oil and 2 parts of phosphoric acid under reflux for 6 hours. The addition of 10 parts of dry hexamethylenetetramine gave a non-reactive resin which was dissolved in 150 parts of turpentine. An additional 10 parts of hexamethylenetetramine were mixed with the solution. The composition yields adherent and resistant coatings when baked on wood or metal. Or it may be used to coat regenerated cellulose films or threads to give insulating material.<sup>70</sup> Plastics for electrical insulation are formed by employing the same reaction with different proportions of reacting materials.<sup>71</sup> These products may also be used as binders for abrasives in grinding-tools,<sup>72</sup> or, dispersed in tetrahydronaphthalene, as an ingredient in printing ink,<sup>73</sup> or mixed with gelatinizable cotton flock as a molding composition.<sup>74</sup>

Modification of the above-mentioned coating composition by the addition of other resins gives a film which dries quickly without the aid of heat.<sup>75</sup> For example, 100 parts of formalin and 50 parts of rosin are added to the non-reactive resin obtained by Byck. The solution is heated under reflux for 5 hours and finally boiled until the water has evaporated. The resin when dissolved in turpentine or toluene gives an air-drying varnish. Incorporation of 5-10 per cent cellulose nitrate or other esters with a solution of the resin just described has been suggested.<sup>76</sup>

The combination of drying oil and rosin as a modifier was also recommended by Mabey.<sup>77</sup> The initial condensation product of 100 parts phenol and 100 parts aldehyde was heated at about 100°C. with rosin (100 parts) and tung oil (6-50 parts) until a homogeneous mass was formed.

Another variation has been proposed by Delaney.<sup>78</sup> To a dehydrated viscous cresol-formaldehyde-tung oil condensation product is added chlorinated naphthalene and the material is heated under reflux until an intimate mixture is obtained. Toluene and xylene are incorporated to form a varnish.

Colloidal dispersions of phenol-oil-formaldehyde resins in butyl alcohol have been employed where varnishes of low penetrative power are required.<sup>79</sup> For the same purpose, Courtney<sup>80</sup> has recommended an emulsion of an oil-synthetic resin varnish in water. A phenol-acetaldehyde condensation product dissolved in oil with the addition of hexamethylenetetramine is used as a binding agent for 1930, 24, 4175. British P. 358,603, 1930; *Chem. Abs.*, 1932, 26, 4970. French P. 700,063, 1930; *Chem. Abs.*, 1931, 25, 3503. A varnish of this nature is suggested for waterproof backings for adhesive tape. See British P. 388,556, 1933, to Johnson & Johnson; *Chem. Abs.*, 1933, 27, 5908. British P. 387,125, 1933; *Chem. Abs.*, 1933, 27, 5484.

<sup>70</sup> H. L. Bender, U. S. P. 1,953,892, Apr. 3, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 3813. British P. 355,318, 1929; *Chem. Abs.*, 1932, 26, 5755.

<sup>71</sup> F. Groff, British P. 367,045, 1929, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 2320. British P. 365,100, 1929; *Chem. Abs.*, 1933, 27, 1775. French P. 689,126, 1930; *Chem. Abs.*, 1931, 25, 1046. British P. 354,166, 1929; *Chem. Abs.*, 1932, 26, 3943. Canadian P. 309,679, 1931; *Chem. Abs.*, 1931, 25, 3138. F. Seebach, German P. 587,876, 1933; *Chem. Abs.*, 1934, 28, 1823.

<sup>72</sup> British P. 356,188, 1930, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 392. French P. 698,090, 1930; *Chem. Abs.*, 1931, 25, 3145.

<sup>73</sup> British P. 408,658, 1932, to Bakelite Corp.; *Brit. Chem. Abs. B.*, 1934, 546.

<sup>74</sup> F. Groff, British P. 354,166, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B.*, 1931, 934. French P. 699,563, 1930; *Chem. Abs.*, 1931, 25, 3449.

<sup>75</sup> V. H. Turkington, U. S. P. 1,877,417, July 17, 1928, to Bakelite Corp.; *Brit. Chem. Abs. B.*, 1928, 681. British P. 293,453, 1928; *Brit. Chem. Abs. B.*, 1930, 204. British P. 324,025, 1927; *Chem. Abs.*, 1930, 24, 3387. British P. 359,986, 1930; *Chem. Abs.*, 1933, 27, 435. French P. 653,004, 1929; *Chem. Abs.*, 1929, 23, 3821. Canadian P. 313,445, 1931, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 4724.

<sup>76</sup> V. H. Turkington, U. S. P. 1,954,836, Apr. 17, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 3921. British P. 342,286, 1929; *Brit. Chem. Abs. B.*, 1931, 405. French P. 684,747, 1929; *Chem. Abs.*, 1930, 24, 5517. Canadian P. 317,205, 1931; *Chem. Abs.*, 1932, 26, 1460. German P. 600,579, 1934; *Chem. Abs.*, 1934, 28, 7562.

<sup>77</sup> H. E. Mabey, British P. 419,883, 1933, to British Resin Products, Ltd.; *Brit. Chem. Abs. B.*, 1935, 112.

<sup>78</sup> M. E. Delaney, U. S. P. 1,980,258, Nov. 13, 1934, to Bakelite Corp.; *Chem. Abs.*, 1935, 29, 366. See also French P. 688,303, 1930; *Chem. Abs.*, 1931, 25, 833.

<sup>79</sup> H. L. Bender, British P. 349,599, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B.*, 1931, 729. French P. 690,457, 1930; *Chem. Abs.*, 1931, 25, 1109. H. F. Wakefield, U. S. P. 1,756,287, Apr. 29, 1930; *Chem. Abs.*, 1930, 24, 8122. British P. 358,603, 1930; *Brit. Chem. Abs. B.*, 1932, 31. Canadian P. 315,010, 1931; *Chem. Abs.*, 1932, 26, 1810. French P. 700,063, 1930; *Chem. Abs.*, 1931, 25, 3503.

<sup>80</sup> R. P. Courtney, U. S. P. 1,987,549, Jan. 8, 1935, to Bakelite Corp.; *Chem. Abs.*, 1935, 29, 1639.

laminated stock such as paper or asbestos.<sup>87</sup> Still another method of obtaining a heat-hardenable resin dissolved in a drying oil has been given.<sup>88</sup> A mixture of Novolak and linseed oil is heated to 300°C. After cooling to 100°C., 3 per cent of hexamethylenetetramine is added and heat again applied. The resulting material hardens at 120°C. within a day.

Potentially reactive phenol-aldehyde resins when heated at 150°C. with oxidized drying oils in a mutual solvent (e.g., cyclohexanol) give on evaporation of the solvent a viscous mass. This, mixed with turpentine, affords a satisfactory varnish film.<sup>89</sup> The presence of iodine accelerates the reaction.<sup>90</sup> An analogous procedure is that suggested by Drummond and Morgan.<sup>91</sup> A phenol and an aldehyde are allowed to react in a volatile solvent and an oil later incorporated. For example, 32 parts of cresol are condensed with 14 parts of formaldehyde in butyl alcohol containing sodium hydroxide. The product is acidified with boric acid and distilled until the boiling point indicates that all the water has been removed.<sup>92</sup> Then 32 parts of tung oil are added and distillation continued until a drop of the solution dries clear.<sup>92a</sup> Material which has been prepared in this manner may be treated with acetic anhydride to give a rapid-drying coating.<sup>93</sup> For instance, 100 parts of resol are allowed to react with 100 parts of tung oil in the presence of 200 parts of cyclohexanol. Most of the solvent is distilled off *in vacuo* and 100 parts of acetic anhydride are added. After the solution is boiled for about 2 hours, the acetic acid formed and the unconverted acetic anhydride are removed as completely as possible by vacuum distillation. The residue is redissolved in cyclohexanol (recovered in the first step of the operation) and the solvent again removed by distillation. The purpose of this procedure is to eliminate the last traces of acetic anhydride. The resin is soluble in an alcohol-benzene mixture, in benzene or in turpentine.

Polyhydric alcohols which have been partially esterified with a drying oil acid may be condensed with an aldehyde and a phenol.<sup>94</sup> Thus resorcinol, paldehyde, tung oil monoglyceride, butyl alcohol and a solution of sodium hydroxide in methylated spirit are heated together. The product diluted with butyl alcohol serves as a varnish.

Condensation of phenol and formaldehyde may be effected by adding hot linseed (or castor) oil to a cold, well-stirred aqueous solution of the reactants.<sup>95</sup> On standing, the mixture separates into two portions, a lower water layer and a

<sup>87</sup> S. E. Chubb, British P. 392,226, 1933, to Bakelite, Ltd.; *Chem. Abs.*, 1933, 27, 4943.

<sup>88</sup> F. Seebach, U. S. P. 1,988,465, Jan. 22, 1935, to Bakelite G. m. b. H.; *Chem. Abs.*, 1935, 29, 1540.

<sup>89</sup> British P. 349,931, 1930, to Bakelite G. m. b. H.; *Brit. Chem. Abs. B.*, 1931, 769. British P. 355,827, 1930; *Brit. Chem. Abs. B.*, 1931, 1019. French P. 690,335, 1930; *Chem. Abs.*, 1931, 25, 1109. British P. 368,807, 1929, addn. to 295,335; *Chem. Abs.*, 1933, 27, 2318. See also F. Seebach, German P. 517,445, 1929, to Bakelite G. m. b. H.; *Chem. Abs.*, 1931, 25, 2311. British P. 409,397, 1934, to Chem. Fabr. K. Albert G. m. b. H.; *Chem. Abs.*, 1934, 28, 6330. French P. 745,316, 1933; *Chem. Abs.*, 1933, 27, 4430.

<sup>90</sup> F. Seebach, U. S. P. 1,985,264, Dec. 25, 1934, to Bakelite G. m. b. H.; *Chem. Abs.*, 1935, 29, 1180. German P. 533,798, 1930, *Chem. Abs.*, 1932, 26, 862.

<sup>91</sup> A. A. Drummond and H. H. Morgan, British P. 329,313, 1928, to Imperial Chem. Ind. Ltd.; *Chem. Abs.*, 1930, 24, 5517. British P. 413,718, 1932, *Brit. Chem. Abs. B.*, 1934, 897. French P. 683,290, 1930; *Chem. Abs.*, 1930, 24, 4648.

<sup>92</sup> H. F. Wakefield (U. S. P. 1,997,614, Apr. 16, 1935, to Bakelite Corp.) suggests that reaction between formaldehyde and phenol-tung oil condensate be effected in high-boiling solvents such as butanol, amyl alcohol, or Cellosolve. Water formed during reaction forms a constant-boiling mixture with the solvent and may be removed as such.

<sup>92a</sup> The drying rate of phenol-resin varnishes is accelerated by adding mixtures of castor oil or tung oil with salts of a dehydrating nature, e.g., the chlorides of iron, zinc, tin, aluminum or calcium. See, A. A. Drummond and H. H. Morgan, British P. 345,633, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 323. German P. 575,920, 1933; *Chem. Abs.*, 1933, 27, 5995.

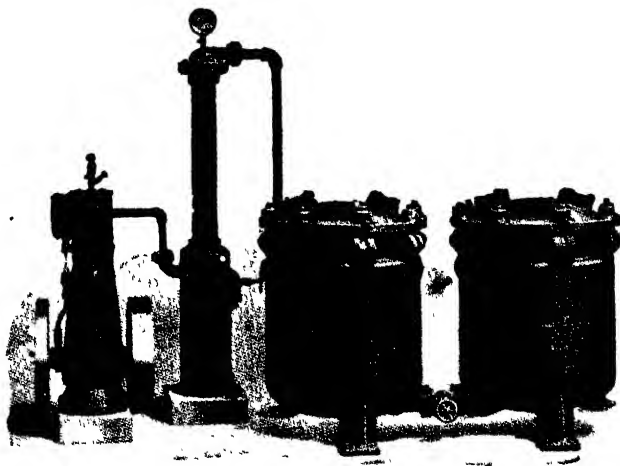
<sup>93</sup> E. Elbel and F. Seiter, U. S. P. 1,963,973, June 26, 1934, to Bakelite G. m. b. H.; *Chem. Abs.*, 1934, 28, 5264. Coating compositions comprising a compound of a heat-hardening phenol-aldehyde resin (resol), an air-drying fatty oil, and acid anhydrides or chlorides, are described by F. Seebach, U. S. P. 1,998,098, Apr. 16, 1935, to Bakelite G. m. b. H.

<sup>94</sup> A. A. Drummond and H. H. Morgan, British P. 413,718, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 253.

<sup>95</sup> A. H. Brown, British P. 255,516, 1925, to Siluminite Insulator Co., Ltd.; *Brit. Chem. Abs. B.*, 1926, 838.

supernatant oil layer. The latter may be decanted and further thickened by heating. If the last operation is carried too far, the hardness of the product may be reduced by the addition of phenol. Reaction between a mixture of 4 parts of naphthol and 50 parts of oxidized castor oil and a mixture of 2.5 parts of hydrochloric acid and 20 parts of formalin at 100°C. yields an elastic body.<sup>96</sup> A resinous material for dressing fabrics was secured by heating equivalent amounts of castor oil and resorcinol below 100°C. Sulphuric acid served as the catalyst.<sup>97</sup>

Phenol-aldehyde condensation products which contain 20 per cent tung oil are soluble in ketones, alcohols, and esters. They can be made soluble in hydrocarbons by heating at 150°C. according to Drummond and Morgan.<sup>98</sup>



*Courtesy Buffalo Foundry & Machine Company*

FIG. 69.—Vacuum-Pressure Impregnating Kettles. The material to be impregnated is placed in the middle container and is dried under vacuum. The right-hand container is filled with a solution of the resin used for impregnation. Upon opening the connecting valve between the two vessels the solution floods the middle vessel. Air pressure can be applied to force the solution into the pores of the material which is being impregnated.

It has been stated that phenol-oil-formaldehyde resins can be employed to improve the strength and wear-resisting qualities of fire hose, rubber tires, or other rubber-coated fabrics.<sup>99</sup> The fabric is first impregnated with the resin and then coated with rubber. Stencil paper is made by coating yoshino paper with a solution of phenol-tung oil-formaldehyde resin, aluminum stearate, and butyl phthalate. The paper is then heated at 140°C. to polymerize the resin.<sup>100</sup>

Tests made on plain and parkerized (treated with phosphoric acid) iron plate, which were coated with a primer, and a suspension of lampblack in a tung oil-phenol-formaldehyde resin, and dipped in a 3 per cent sodium chloride solution, showed that the attack was greatest at the air-liquid interface. Resistance de-

<sup>96</sup> A. Caroselli, U. S. P. 1,086,139, Feb. 3, 1914, to Chem. Fabr. Flörsheim H. Noerdlinger; *J.S.C.I.*, 1914, 33, 269. German P. 253,517, 1910; *J.S.C.I.*, 1913, 32, 36.

<sup>97</sup> Swiss P. 169,563, 1934, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1935, 29, 2000.

<sup>98</sup> A. A. Drummond and H. H. Morgan, British P. 345,310, 1929, to Imperial Chem. Ind. Ltd.; *Chem. Abs.*, 1932, 26, 324.

<sup>99</sup> British P. 356,818, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 1046.

<sup>100</sup> K. W. Carr, U. S. P. 1,894,731, Jan. 17, 1933, to Ditto, Inc.; *Brit. Chem. Abs. B*, 1933, 960. U. S. P. 1,878,672, Sept. 20, 1932; *Brit. Chem. Abs. B*, 1933, 621.

creased with increasing oil content.<sup>101</sup> For insulating copper wire, Ruben<sup>102</sup> employed a phenol-oil-formaldehyde resin (in a very thin film) to act as a binder for a coating of insulating oxides such as those of titanium, chromium or iron.

### OTHER OIL-SOLUBLE RESINS

Although real success was achieved in the search for oil-soluble phenol resins by modifying them with drying oils or with natural resins, some need was shown for producing oil-soluble resins directly without such modification. As will be seen from the discussion that follows, this need was filled partially by the use of phenolic substances other than ordinary phenol.<sup>103</sup>

Some of the first unmodified oil-soluble resins were produced from the condensation of formaldehyde with o-cresol<sup>104</sup> or p-cresol.<sup>105</sup> Others have been obtained by allowing acetaldehyde<sup>106</sup> to react with tar oils<sup>107</sup> or with phenol in carbon tetrachloride and catalyzed with hydrochloric acid.<sup>108</sup> The use of phenols of high molecular weight also yield the desired products.<sup>109</sup> Substances soluble in aromatic hydrocarbons, turpentine, and fatty oils have been made by heating a phenol ether (e.g., anisole or  $\beta$ -naphthol ethyl ether), with formaldehyde in the presence of a strong organic acid (formic) or an inorganic salt with an acid reaction (zinc chloride).<sup>110</sup> Condensation has also been carried out with the methyl or ethyl ether of 1,3,5-xylenol.<sup>111</sup> Coating compositions are made from the resultant product by incorporation with drying oils or nitrocellulose.

The addition of diazotized p-nitroaniline to a molten mixture of 94 parts of phenol and 7.5 parts of hexamethylenetetramine gives an oil-soluble dyestuff.<sup>112</sup> On cooling, the mass is converted into a solid metallic-green- or orange-colored azo resin, which gives orange-colored solutions in oils and fats.

When the reaction between phenol and formaldehyde is carried out in the presence of a terpenic or alicyclic alcohol such as  $\alpha$ -terpineol, a fusible resin soluble in oils results.<sup>113</sup>

Varnish resins of the oil-soluble type are obtained by the reaction of xylenols with paraformaldehyde, according to Drummond and Morgan.<sup>114</sup> For example 976 parts of mixed xylenols, 150 parts of paraformaldehyde, 30 parts of concentrated hydrochloric acid and 1000 parts of methyl alcohol are boiled together for 20 hours. The product is distilled at 120°C. until the residue becomes hard on cooling. The latter may be dissolved in an equal weight of tung oil by heating at 175°C. for 2 hours and used with solvent naphtha as a varnish. Later work indicated the fractions

<sup>101</sup> F. Kolke, *Farben-Ztg.*, 1934, 39, 331, *Brit. Chem. Abs. B*, 1934, 413.

<sup>102</sup> S. Ruben, U. S. P. 1,896,040 to 1,896,043, Jan. 31, 1933, to Vega Mfg. Corp.; *Chem. Abs.*, 1933, 27, 2507.

<sup>103</sup> A detailed treatment of this type of resin is found in Chapter 17.

<sup>104</sup> J. W. Aylsworth, U. S. P. 1,111,237, Sept. 22, 1914; *Chem. Abs.*, 1914, 8, 3634. See also French P. 334,425, 1907, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1908, 27, 457.

<sup>105</sup> W. T. Robinson-Bindley, A. W. Weller and E. Duleken, *British P.* 134,563, 1918; *J.S.C.I.*, 1920, 39, 35A.

<sup>106</sup> Apparatus especially adapted for the production of phenol-aldehyde-type oil-soluble resins is described by A. Johnson, U. S. P. 1,994,714, Mar. 19, 1933, to Combustion Utilities Corp. Provision is made for the immediate return to the reaction kettle of volatilized low-boiling ingredients (e.g., acetaldehyde) and their thorough intermixture with the less volatile liquids. A better control of the process is thus ensured, with less danger of the formation of an oil-insoluble product.

<sup>107</sup> *British P.* 156,740, 1921, to Chem. Fabr. Worms A.-G.; *Chem. Abs.*, 1921, 15, 1821.

<sup>108</sup> A. Steindorff and G. Balle, *German P.* 365,286, 1920, to Farb. vorm. Meister, Lucius & Brünning; *J.S.C.I.*, 1923, 42, 614A.

<sup>109</sup> H. H. Morgan, *J. Oil and Colour Chem. Assoc.*, 1932, 15, 106; *Chem. Abs.*, 1932, 26, 3941.

<sup>110</sup> *German P.* 406,152 and 406,999, 1919, and 407,000, 1920, to Farb. vorm. Meister, Lucius & Brünning; *J.S.C.I.*, 1925, 44, 461B.

<sup>111</sup> R. Hill, *British P.* 400,272, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 2206.

<sup>112</sup> H. Plauson, U. S. P. 1,500,844, July 8, 1924; *J.S.C.I.*, 1924, 43, 720B. H. Plauson and J. A. Vielle, *British P.* 182,497, 1921; *J.S.C.I.*, 1922, 41, 676A.

<sup>113</sup> I. Rosenblum, *British P.* 416,476, 1932; *Brit. Chem. Abs. B*, 1934, 1022. *French P.* 738,444, 1932; *Chem. Abs.*, 1933, 27, 1775.

<sup>114</sup> A. A. Drummond and H. H. Morgan, *British P.* 345,276, 1929, to Imperial Chem. Ind. Ltd.; *Brit. Chem. Abs. B*, 1931, 636.

of low-temperature tar boiling above 230°C. yield resins which may be incorporated in tung oil,<sup>115</sup> or alternatively the phenolic fraction (100 grams) boiling at 255-275°C. may be condensed with paraformaldehyde (40 grams). When the mixture is heated, a vigorous reaction occurs at 110-120°C.; and further heating is necessary until a clear melt is obtained. More aldehyde should be added at this point to combine with unreacted phenol. The resultant brown resin has a melting point of about 150°C. Other investigators<sup>116</sup> have incorporated fatty acids in the reaction of xylenols or higher phenols with formaldehyde.

The preparation of oil-soluble resins from cresylic acid and formaldehyde is described by Novak.<sup>117</sup> Three parts each of cresylic acid and commercial 40 per cent formaldehyde are mixed with 1 part of ammonium hydroxide (sp.gr. 0.898). After the reaction has been completed, which may take 30-60 minutes, the aqueous layer is decanted. The product obtained contains 3-5 per cent nitrogen according to Novak. It is converted into a varnish by heating with two-thirds its weight of tung oil at 90-100°C. The resulting solution is used to impregnate cloth, fibers or paper to form insulating material. It is stated that the varnish heat-hardens very quickly to an infusible state.

It has been noted that crystalline condensation products obtained from  $\beta$ -naphthol and formaldehyde are made oil-soluble by heating them above their melting points. A solution of such substances in fatty oils is said to give good varnishes.<sup>118</sup> Similarly a fusible phenol-aldehyde resin may be heated with a polynuclear phenol to yield a material that is oil-soluble.<sup>119</sup> For example, 100 kilos of reactive resin are fused with  $\beta$ -naphthol and heated for 1.5 hours at 260°C. If manganese oxide or lead oxide is used as a catalyst, the resin is more soluble in oil, and the varnish dries more quickly. Addition of natural resins such as rosin, dammar, and copal facilitates solution in oils.<sup>120</sup>

According to Seebach<sup>121</sup> the same procedure is applicable to infusible phenol resins. Equal parts of resite and dihydroxybiphenyl are heated together until the resin is dissolved and no more water vapor is driven off. The resulting product is readily soluble in hot fatty oils.

Investigations of the effect of  $\beta$ -naphthol on the drying rate of an oil show that it accelerates the rate at elevated temperatures in sunlight. However retardation takes place in indirect light, unless a drier is present. The drying of varnishes made from tung oil and an acid or neutral resin is retarded or accelerated respectively by  $\beta$ -naphthol; but if a drier is also present, retardation is usually observed.<sup>122</sup> The addition of 0.3-1 per cent of cresol to an oil varnish is said to prevent skinning.<sup>123</sup> Merkle<sup>124</sup> noted that the presence of an oxidation catalyst (manganese or lead) and an inhibitor (eugenol or  $\alpha$ -naphthol) in drying-oil compositions prevents their oxidation in bulk without retarding their normal drying rate in thin films.

Condensation of hydroxybiphenyls with formaldehyde in the presence of fatty

<sup>115</sup> E. L. Holmes, *J S C.I.*, 1934, 53, 74T. See also Chapter 12.

<sup>116</sup> V. H. Turkington and W. H. Butler, Canadian P. 306,936, 1930, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 834.

<sup>117</sup> I. J. Novak, U. S. P. 1,952,725, Mar. 27, 1934, to Raybestos-Manhattan, Inc.; *Chem. Abs.*, 1934, 28, 3605. British P. 334,232, 1929; *Brit. Chem. Abs. B*, 1930, 1039.

<sup>118</sup> German P. 468,391, 1925, to Bakelite G.m.b.H.; *Chem. Abs.*, 1929, 23, 1294.

<sup>119</sup> F. Seebach, U. S. P. 1,944,016, Jan. 16, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 2205. U. S. P. 1,809,732, Jan. 9, 1931; *Chem. Abs.*, 1931, 25, 4422. German P. 494,709, 1926; *Chem. Abs.*, 1930, 24, 3662. German P. 544,894, 1927; *Chem. Abs.*, 1932, 26, 3687. British P. 282,414, 1926; *Chem. Abs.*, 1928, 22, 3791.

<sup>120</sup> F. Seebach, U. S. P. 1,844,824, Feb. 9, 1932, to Bakelite G.m.b.H.; *Chem. Abs.*, 1932, 26, 2073. German P. 530,208, 1927; *Chem. Abs.*, 1932, 26, 325. British P. 283,124, 1927; *Chem. Abs.*, 1928, 22, 3999. French P. 645,713, 1927; *Chem. Abs.*, 1929, 23, 2051.

<sup>121</sup> F. Seebach, U. S. P. 1,971,507, Aug. 28, 1934, to Bakelite G. m. b. H.; *Chem. Abs.*, 1934, 28, 6580. <sup>122</sup> C. A. Thomas and P. E. Marling, *Ind. Eng. Chem.*, 1932, 24, 871. See also R. S. Hilpert and C. Niehaus, *Angew. Chem.*, 1934, 47, 86; *Chem. Abs.*, 1934, 28, 2549.

<sup>123</sup> J. K. Hunt and G. H. Latham, U. S. P. 1,948,562, Feb. 27, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1934, 1070.

<sup>124</sup> C. R. E. Merkle, U. S. P. 1,829,999, Nov. 3, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 860.

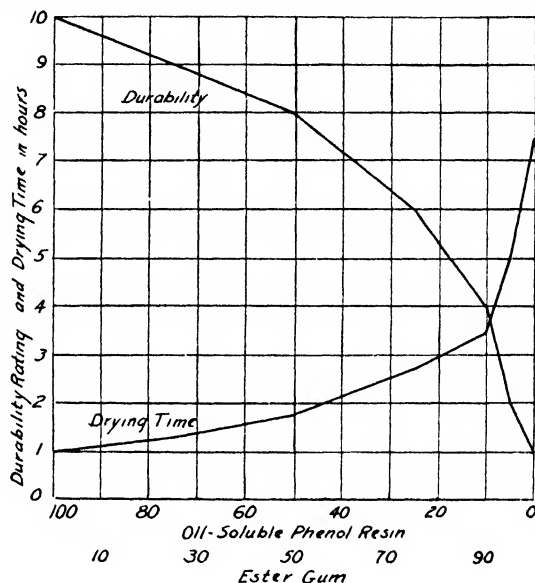


oils yields oil-soluble resins.<sup>125</sup> A mixture of 100 parts of p-hydroxybiphenyl<sup>126</sup> and 100 parts of formalin are heated until a resin forms. This is heated with 100 parts of tung oil at 210°C. until a small portion remains clear on cooling and can be diluted with cold linseed oil. Addition of more oil, while keeping the temperature above 200°C., a thinner, and a drier gives a varnish. This composition, or one made from the resin prepared by Byck,<sup>127</sup> is said to be superior to a varnish containing ester gum in that it dries more quickly, the films are harder, more elastic, and more durable.<sup>128</sup> (See Figs. 70 and 71).

The data for the curves were obtained from a mixture of 1 part resin and 2 parts tung oil. Elasticity was determined by the standard test of adding Kauri

FIG. 70.

Drying-Time of Varnishes and Durability of Films Prepared from Mixtures of Ester Gum and Oil-Soluble Phenol Resin. (V. H. Turkington.)



gum and finding the amount of such addition necessary to produce cracks on bending around a 3 mm. rod after baking 5 hours at 95°C. The durability rating indicates the relative freedom from cracks or other signs of failure after exposure of test panels. Hardness figures were obtained with a swinging-beam apparatus.

Coatings made in the same manner, except that air was bubbled through the mixture during heating, are recommended for treating floor coverings.<sup>129</sup>

<sup>125</sup> V. H. Turkington and W. H. Butler, British P. 347,737, 1929, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 1812. French P. 689,014, 1930; *Chem. Abs.*, 1931, 25, 1109. German P. 571,039, 1930; *Chem. Abs.*, 1933, 27, 2831. Cf. French P. 716,510, 1931; *Chem. Abs.*, 1932, 26, 2333.

<sup>126</sup> Hydroxybiphenyls are prepared from the corresponding chlorobiphenyl by hydrolysis with aqueous sodium hydroxide under pressure at 250–300°C. employing a copper catalyst (E. C. Britton, U. S. P. 1,959,283, May 15, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1934, 28, 4433). R. W. Rittler (German P. 605,520, 1934, to Chemische Fabrik von Heyden A.-G.; *Chem. Abs.*, 1935, 29, 1836) recommends separation of o- and p- forms of hydroxybiphenyls by treatment with aqueous solutions of alkaline earth salts, hydroxides or oxides and filtering. o-Hydroxybiphenyl is soluble and may be precipitated from the filtrate by acidification. Phenol and chlorocyclohexane react at 300°C. to give o- and p-cyclohexyl phenol (E. C. Britton and R. P. Perkins, U. S. P. 1,862,075, June 7, 1932, to Dow Chemical Co.; *Chem. Abs.*, 1932, 26, 4068). The latter compound when heated with a dehydrogenating catalyst yields o- or p-phenyl phenol (E. C. Britton and S. L. Bass, U. S. P. 1,862,000, June 7, 1932, to Dow Chemical Co.; *Chem. Abs.*, 1932, 26, 4068).

<sup>127</sup> L. C. Byck, U. S. P. 1,590,079, June 2, 1926, to Bakelite Corp.; *Chem. Abs.*, 1926, 20, 3090. This has been discussed previously in the chapter.

<sup>128</sup> V. H. Turkington and W. H. Butler, U. S. P. 1,988,615, Jan. 22, 1935, to Bakelite Corp.; *Chem. Abs.*, 1935, 29, 1667. British P. 378,094, 1931; *Brit. Chem. Abs.*, B, 1932, 997. V. H. Turkington, R. C. Shuey and W. H. Butler, *Ind. Eng. Chem.*, 1930, 22, 1177. G. Dring, *J.S.C.I.*, 1934, 53, 1013. See also *Circ. Natl. Paint, Varnish, Lacquer Assoc.*, 1934, 471, 297; *Chem. Abs.*, 1935, 29, 363.

<sup>129</sup> V. H. Turkington, U. S. P. 1,988,616, Jan. 22, 1935, to Floor Covering Patents, Inc.; *Chem. Abs.*, 1935, 29, 1667.

In a somewhat analogous procedure<sup>120</sup> a mixture of  $\alpha,\alpha(4,4'$ -dihydroxy-3,3'-dimethyldiphenyl) cyclohexane, or  $\beta,\beta(4,4'$ -dihydroxy-3,3'-dimethyldiphenyl) propane, and formaldehyde is condensed in the presence of hydrochloric acid and denatured alcohol. The product may be dissolved in tung oil to give a varnish.

The reaction of a phenol with a ketone yields a compound which is converted into an oil-soluble resin by treatment with formaldehyde.<sup>121</sup> Equimolecular amounts of phenol and acetone, using hydrochloric acid as a catalyst, form  $\beta,\beta$ -bis(4-hydroxy-phenyl) propane and a condensation product of acetone with

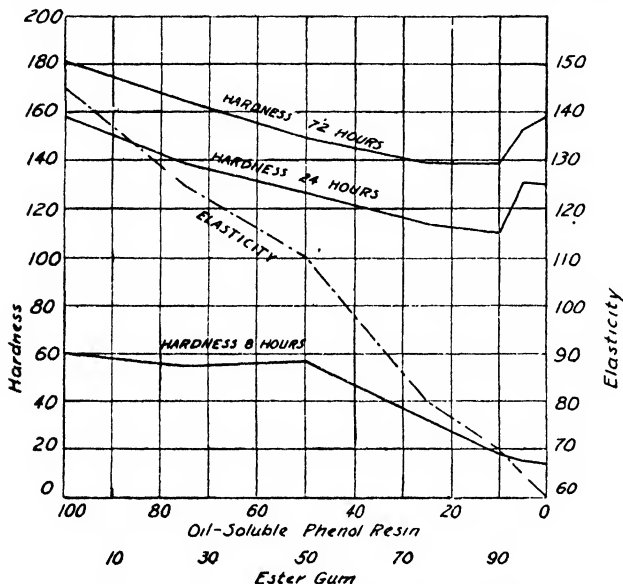
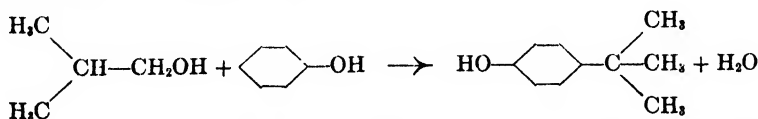


FIG. 71.  
Hardness and Elasticity of Varnish Films Containing Mixtures of Oil-Soluble Phenol Resin and Ester Gum. (V. H. Turkington.)

the latter. The mixture is refluxed for 8 hours with a 40 per cent solution of formaldehyde (0.35 mol per mol of phenol used in the first reaction). Water and excess formaldehyde are removed by distillation *in vacuo*. at 200°C. The resulting resin has a melting point of 100-110°C. and is soluble in tung and other oils.

In some instances oil-soluble resins are made by condensation of aldehydes with phenols containing an alkyl or aryl group in the para position. Such phenol derivatives are obtained by heating alcohols with phenols in the presence of zinc chloride or other dehydrating agents.<sup>122</sup> Thus by heating isobutyl alcohol and phenol, the following reaction occurs:



<sup>120</sup> A. Hill, R. Hill, and E. E. Walker, British P. 401,309, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 2554.

<sup>121</sup> K. M. Irey, U. S. P. 1,948,469, Feb. 20, 1934, to Resinox Corp.; *Chem. Abs.*, 1934, 28, 2923. U. S. P. 1,970,912, Aug. 21, 1934; *Chem. Abs.*, 1934, 28, 6330.

<sup>122</sup> A. Liebmann, *Ber.*, 1881, 14, 1842; 1882, 15, 180. M. Senkowski, *Ber.*, 1890, 23, 2412. H. Auer, *Ber.*, 1884, 17, 669. B. Fischer and B. Glütner, *Ber.*, 1893, 26, 1646. German P. 17,311, 1881, to A.-G. für Anilinfabr.; *J.S.C.I.*, 1882, 1, 226. L. v. Dobrzycki, *J. prakt. Chem.*, 1887, 36, 389; *Chem. Zentr.*, 1887, 1494. German P. 23,775, 1882, to A.-G. für Anilinfabr.; *J.S.C.I.*, 1884, 3, 105. H. Mevei and K. Bernhauer *Monatsh.*, 1929, 53-54, 731; *Chem. Abs.*, 1930, 24, 346. O. Hinsberg, German P. 589,376, 1930; *Chem. Abs.*, 1932, 26, 1617. E. C. Fanto, U. S. P. 1,824,426, Sept. 22, 1931, to McKesson and Robbins, Inc.; *Brit. Chem. Abs. B*, 1933, 219. R. R. Read, U. S. P. 1,887,662, Nov. 15, 1932, to Sharp & Dohme, Inc.; *Brit. Chem. Abs. B*, 1933, 999.

Phenols can be alkylated with an alkyl halide in the presence of zinc or ferric chloride,<sup>133</sup> or of alcoholic potassium hydroxide.<sup>134</sup> The reaction will also take place with an unsaturated hydrocarbon such as isobutylene both with<sup>135</sup> and without<sup>136</sup> metallic halides as catalysts. Thomas<sup>137</sup> has made p-tertiary amyl phenol by allowing phenol to react with amylene in the presence of sulphuric acid. Similarly octenes, obtained from the isomeric butenes, react with phenols or phenyl ethers in the presence of sulphuric acid to give the corresponding alkylated compound.<sup>138</sup>

Analogous aryl-substituted phenols such as triphenyl-p-hydroxy-phenyl-methane [ $(C_6H_5)_3CC_6H_4OH$ ] have been prepared by elimination of water between triphenylcarbinol and phenol<sup>139</sup> and by the Friedel-Crafts reaction, using triphenyl-chloromethane and phenol.<sup>140</sup>

The preparation of resins with p-alkylated phenols is described by Hönel.<sup>141</sup> Eighty-two g. of p-tertiaryamylphenol, 90 g. of 30 per cent formaldehyde, and 75 cc. of 3N sodium hydroxide are dissolved by gentle warming and heated at 50-55°C. for 24 hours. The viscous oily reaction product is precipitated with an acid, separated from the supernatant liquid, and dried. The resultant resin is fast to light and soluble in oils.<sup>142</sup> The reaction may also be carried out in an acid medium.<sup>143</sup> Hönel<sup>144</sup> has treated these compounds with esters to form materials for impregnating and coating. For example, 6 parts of melissic palmitate (beeswax) were melted and stirred with the liquid condensate obtained from 1 part of p-tertiaryamylphenol and 1 part of 30 per cent formaldehyde. The temperature was gradually raised to 240°C. The brown end-product was harder than beeswax, more plastic, and surfaces coated with it were more easily polished. It is contended that p-substituted phenol resins go quite slowly into the infusible state. Better control of the reaction is thus permitted and an advantage in the preparation of oil-soluble bodies is indicated.<sup>145</sup>

Cyclohexyl phenol may be used instead of an alkylated phenol in the condensations just discussed.<sup>146</sup> For example, p-cyclohexyl phenol is heated with formaldehyde and oxalic acid. The product heated with tung oil and dissolved in solvent naphtha gives a coating composition. It may also be dissolved with nitrocellulose

<sup>133</sup> A. Gurewitsch, *Ber.*, 1899, 32, 2424.

<sup>134</sup> E. W. Lewis, *J.C.S.*, 1903, 83, 329.

<sup>135</sup> F. Linner, U. S. P. 1,892,990, Jan. 3, 1933, to Beck, Koller & Co.; *Brit. Chem. Abs.* B, 1934, 54. Austrian P. 124,281, 1931, to Soc. Reichhold Flugger & Boecking; *Chem. Abs.*, 1932, 26, 735. French P. 697,711, 1930; *Chem. Abs.*, 1931, 25, 3013.

<sup>136</sup> W. Koenigs, *Ber.*, 1890, 23, 3144. W. Koenigs and R. W. Carl, *Ber.*, 1891, 24, 3889. W. Koenigs and C. Mai, *Ber.*, 1892, 25, 2649. R. Anschütz and H. Beckerhoff, *Ann.*, 1903, 327, 219; *J.C.S.*, 1903, 84 (1), 556. British P. 308,662, 1928; *Chem. Abs.*, 1930, 24, 378.

<sup>137</sup> C. A. Thomas, British P. 420,636, 1934, to Sharples Solvents Corp.; *Brit. Chem. Abs.* B, 1935, 140. <sup>138</sup> H. Bruson, U. S. P. 1,987,228, Jan. 8, 1935, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1935, 29, 1432.

<sup>139</sup> A. Baeyer and V. Villiger, *Ber.*, 1902, 35, 3013. See also T. Zincke and E. Wugk, *Ann.*, 1908, 363, 288. D. R. Boyd and D. V. Hardy, *J.C.S.*, 1928, 630.

<sup>140</sup> A. Baeyer, *Ber.*, 1909, 42, 2624. M. Busch and R. Knoll, *Ber.*, 1927, 60, 2243, *Chem. Abs.*, 1928, 22, 400.

<sup>141</sup> H. Hönel, U. S. P. 1,800,295, Apr. 14, 1931, to Beck, Koller & Co.; *Chem. Abs.*, 1931, 25, 3503. H. Hönel, J. Ehrenfeld and O. Reichold, British P. 417,122, 1933; *Brit. Chem. Abs.* B, 1934, 1071. French P. 758,861, 1934; *Chem. Abs.*, 1934, 28, 3256. Alkylation of resinous materials which contain an aromatic group makes them soluble in hydrocarbon oils (French P. 771,214, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, 29, 854).

<sup>142</sup> See J. Harlass (*Farben-Ztg.*, 1933, 38, 1466; *Brit. Chem. Abs.* B, 1933, 1068) for a report of impact, bending and resistance to alkali tests with varnishes made from Super Beckacete 1001, a product of Beck, Koller & Co. This type of varnish was recommended (J. Harlass, *Farben-Ztg.*, 1934, 39, 653; *Chem. Abs.*, 1934, 28, 5690) as a coating composition for food cans.

<sup>143</sup> A. Hill, R. Hill and E. E. Walker, British P. 401,290, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 2555.

<sup>144</sup> H. Hönel, U. S. P. 1,800,296, Apr. 14, 1931, to Beck, Koller & Co.; *Chem. Abs.*, 1931, 25, 3503. U. S. P. 1,968,080, July 31, 1934; *Chem. Abs.*, 1934, 28, 5941. British P. 334,572, 1929; *Chem. Abs.*, 1931, 25, 1110. French P. 676,456, 1929; *Chem. Abs.*, 1930, 24, 3092. German P. 565,413, 1929, addn. to 563,870; *Chem. Abs.*, 1933, 27, 2341. German P. 584,858, 1933; *Chem. Abs.*, 1934, 28, 1154.

<sup>145</sup> H. Hönel, U. S. P. 1,996,069, Apr. 2, 1935.

<sup>146</sup> British P. 411,442, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 7044.

in a mixture of toluene, butyl and ethyl acetate, and butyl alcohol with tritolyl phosphate to form a lacquer.

The heavy-metal salts of oil-soluble phenol aldehyde resins have been suggested as siccatives for paints and varnishes.<sup>147</sup> To prepare these salts, phenol-acetaldehyde condensation products are heated with aqueous sodium hydroxide until saponification is complete. Subsequently treatment with hot lead acetate solution precipitates the lead salts, which are separated, dried and dissolved in turpentine. Alternatively, the condensation product may be heated with cobalt acetate until the evolution of acetic acid has ceased.

The use of raw oil rather than heat-thickened tung oil has been recommended with phenol-formaldehyde resins on the grounds that it exerts a greater solvent action on the resin, has greater anti-gelling power and is cheaper.<sup>148</sup>

#### SUMMARY

The development of phenolic resins in the varnish industry may be indicated by the following stages of progress:

1. After the World War the producers of butyl alcohol turned to nitrocellulose lacquers in search of an outlet for that alcohol. The widespread use of lacquers had been greatly hindered by the lack of adequate solvents for nitrocellulose. Butyl acetate was found to be satisfactory for the purpose and a lacquer industry began which, with the advent of nitrocellulose of reduced viscosity, forged ahead at a rapid pace and acquired a very important position in the coating industry.

2. The solubility in oils which was conferred by natural resins (in particular rosin) on phenolic resins which otherwise would be insoluble gave products which from about 1925 onward met commercial requirements sufficiently to be used quite extensively. One of these products was known as Albertol. Another of somewhat later development was Amberol, which was marketed in various forms. Those phenolic resins which contained rosin were found to be less resistant to weathering influences than some of the natural-resin varnish compositions. The fact that the presence of rosin militated against the life of the coating served, at least in some cases requiring exterior exposure, to diminish the scope of utility of resins of that type. However, nitrocellulose lacquers were so fast-drying and were pushing oil varnishes so hard that varnish producers seized upon modified phenol-formaldehyde resins, despite their defects, because these synthetic resins provided a faster drying effect than was possible to obtain with the varnish gums used up to that time.

3. Hydroxybiphenyl, a by-product in making phenol from chlorobenzene, was found to react with formaldehyde to give an oil-soluble resin (without rosin) which, incorporated with drying oils in the varnish-making procedure, provided varnishes of great resistance to exterior exposure.

4. Concurrently, alkylated phenols were made which likewise possessed the characteristic of dissolving in drying oils. These substituted compounds resembled in their behavior in varnish compositions those of the hydroxybiphenyl type and gave such promising results that their manufacture began and has increased to a considerable scale. The alkylated phenols are made either by treating phenol or one of its homologues with alkylated halide in the presence of aluminum chloride or by causing an olefin to combine directly with the phenol in the presence of sulphuric acid or like condensing agent.<sup>149</sup> The resulting alkyl halide is then

<sup>147</sup> H. Rauch, German P. 402,539, 1922; *J.S.C.I.*, 1925, 44, 17B.

<sup>148</sup> W. Ruckert, *Farben-Ztg.*, 1933, 38, 995; *Brit. Chem. Abs.* B, 1933, 676.

<sup>149</sup> For a review of the various methods of making alkyl phenols see Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, especially page 565, *et seq.*

resinified by means of formaldehyde. Thus there is further available an oil-varnish resin group of which the important members are of the *p*-tertiary butylphenol type and the corresponding amyl compound.

Resins from hydroxybiphenyl and from the synthesized alkyl phenols have provided varnishes which possess a sufficiently rapid rate of drying to compete successfully with nitrocellulose lacquers. In addition they give a degree of depth and richness of coating not ordinarily obtainable by lacquers without the application of a greater number of coats.

5. Cheaper forms of oil-soluble phenolic resins are provided by those from xylene, it having been found that xylenols produce resins which have good solubility in drying oils and yield durable varnishes. The color of a xylene resin varnish is not always satisfactory for some purposes, since the coating shows a tendency to darken to a slight extent on exposure to light. Other resins which have been used in making oil varnishes are those derived by the action of phenol on acetone and treatment of the resulting compound with an aldehyde. In general, therefore, the development of resins of the phenolic type adequate for use in making oil varnishes calls either for the addition of the solubilizing agent (rosin) to the resin from phenol itself, or for the substitution in the benzene ring of the phenol structure a sufficient number of hydrocarbon or other groups to impart the needed degree of oil-solubility.

The modified phenol-formaldehyde resins undoubtedly have a tendency to accelerate the drying of the various oils used in varnish making. The assertion has been made that the phenolic resins stimulate polymerization of the oil with the result that the coating sets and becomes dust- and tack-free without the necessity of protracted exposure to oxidation in the air. However, since free phenol and cresol act as anti-oxidants, care must be taken that resins prepared for the varnish industry are so free from substances retarding oxidation that the expected acceleration of drying by virtue of the presence of the phenolic resins is not impaired.

## Chapter 20

# Modified Phenol-Formaldehyde Resins

## II. Various Modifying Agents

Fusible phenol-formaldehyde resins possess neither toughness nor elasticity and are notably brittle. Although the infusible resins are hard and strong, they too are somewhat brittle and possess comparatively little elasticity or flexibility. Efforts to supply these properties have been unremitting. If flexibility could be imparted to the product, a non-inflammable substitute for celluloid in many of its applications could be realized. If tough, rubbery, elastic qualities could be developed its application in the rubber field might follow. In the present chapter there are considered various compositions formed by adding to the phenol-aldehyde reaction mixture or to the partially condensed resin certain substances intended to modify the physical qualities of the product. The discussion, however, does not embrace fillers which are considered in the chapters relating to molding compositions (Chapters 65 and 66). Some of the modifying agents such as tung oil probably enter into chemical combination (see Chapter 19) while others are, to a large extent at least, merely inert additions or diluents. The suggestions covering proposed additions to phenol-formaldehyde resins are so numerous that space does not permit detailed descriptions of all of them. Modifiers may be easily obtainable substances, such as glycerol, dibutyl phthalate, starch, dextrin, glue, gelatin, albumin, natural resins and vegetable ivory, as well as a number that are more rare and less easily obtainable, such as intestinal mucin, a serum from cattle blood, alginic acid, cholesterol and the proteins made from corn and beans.

The use of modifiers has spread in the resinous products industry with each succeeding year. As early patents expired the growth of competition narrowed the margin of profit on the older products and a constant search has been continued for modifying agents which would so alter the original properties of the resin that new fields of use would be opened for it. This has brought a great variety of modifiers to light, some of which have attained commercial importance.

### PROTEIN COMPOSITIONS

Phenol is a powerful solvent for proteins such as glue and casein, and early in the history of the development of phenol-formaldehyde resins various suggestions were made for the solution of a protein in phenol and treatment of the mixture with formaldehyde to form thermoplastic substances. Formaldehyde which reacts with both the phenol and the protein, was supposed to harden them both and to yield a product of improved elasticity.

In 1907 Goldsmith<sup>1</sup> used a mixture of gelatin,  $\beta$ -naphthol and formaldehyde for making a molding composition. He termed the formaldehyde an indurating

<sup>1</sup> B. B. Goldsmith, U. S. P. 1,076,417, Oct. 21, 1913; *J.S.C.I.*, 1913, 32, 1164.

agent, as it gave to the composition greater toughness and increased the resistance to the action of water. Also, it minimized the tendency of the composition to stick to the mold. Stockhausen<sup>a</sup> incorporated gelatin with a phenol resin. A modern application of gelatin-modified resins is a cementing material for laminated glass.<sup>c</sup> Fibers have been made antiseptic, waterproof and lustrous by treatment with a mixture of gelatin, boric acid, paraformaldehyde, a phenolic condensation product, alum and camphor.<sup>d</sup>

Berend<sup>e</sup> described the preparation of a modified phenol-formaldehyde resin which contained glue. For example, 150 parts by weight of glue were dissolved in 75 parts each of phenol and glycerol at 70-80°C., and to this was added a solution of 24 parts of shellac in 48 parts of aniline, and finally 30 parts of paraform or 80 parts of a glycerol-formaldehyde mixture containing about 30 parts of formaldehyde was quickly stirred into the composition. This mixture gradually solidified becoming homogeneous and tough, and was molded before it became completely solid. Berend<sup>e</sup> also used casein. Twenty-five parts by weight each of phenol and casein and 2 parts of caustic soda were mixed and heated until the solution became clear and viscous. Then, 50 parts of phenol and 10 parts of trioxymethylene were added, and the mixture was slowly heated to 100°C. to bring about reaction. Further additions of 10 parts and then 5 parts of trioxymethylene were made at intervals. The mixture was thereafter cautiously heated and maintained in a state of gentle ebullition for a period of about 2 hours until a test sample solidified on cooling in the air. Filling materials were added and the composition placed in molds where it was hardened by heating for 6 hours at 100-110°C. and then for a few hours at a slightly higher temperature.<sup>f</sup> Wiechmann<sup>g</sup> prepared modified phenol-formaldehyde resins by reacting paraform with crystallized phenol, and mixing the product with cellulose or albumin. The product was soluble in a mixture of methyl and amyl alcohols, and was useful as a varnish. It was convertible into an insoluble infusible body by the action of heat.

Tarasov<sup>h</sup> added numerous substances to phenol-formaldehyde resins, for the purpose of reducing inherent brittleness. Thus, a mixture of 100 parts by weight phenol, 20 parts egg albumin, 50 parts water, 57 parts of a 37 per cent aqueous solution of sulpho-acids produced from petroleum acid sludge, was heated to 80°C. until the albumin dissolved and about 50 parts of the water had evaporated. Then, the mixture was cooled and 40 parts of formalin solution added. On heating to 80°C. rather violent ebullition occurred on account of the reaction of condensation. Evaporation was resumed, another 50 parts of water removed, the mix cooled to 25°C. and 50 parts of formalin solution introduced. The mixture was now a rather thick liquid. It was poured into a mold and allowed to stand for 12 hours. During this time it became nearly solid. The molds were placed in a bath of water at 75°C. for a half hour, then heated to 90°C. for 1 or 2 hours and finally to 100°C. for the same length of time. The product was an infusible, opaque, yellowish, elastic solid.

Kühl<sup>i</sup> heated cresol and casein with formaldehyde, with or without a small quantity of potassium carbonate, in an autoclave at 3-5 atmospheres pressure. For example, 250 grams of granular casein were soaked in 500 g. of cresol until a uniform mass was obtained. To this was added 400 g. of formaldehyde and the mixture was heated in an autoclave and kept at a pressure of 3 atmospheres for 10 minutes. The product was dissolved in alcohol to form a varnish. According to Nakanishi<sup>j</sup> casein may be dissolved in a concentrated solution of borax and dissolved in 10-20 parts of alcohol. Phenol and formalin were heated with sodium acetate under reflux at about 100°C. for 2 hours and diluted with 20 parts of alcohol. By mixing this with the previously prepared casein solution, a varnish of rich luster was made. A substitute for hard rubber proposed by Parkert is made from mica 35 parts, galalith powder (artificial

<sup>a</sup> J. Stockhausen, U. S. P. 1,061,881, May 13, 1913; *Chem. Abs.*, 1913, 7, 2319. French P. 466,435, 1913; *J.S.C.I.*, 1914, 33, 605.

<sup>b</sup> P. R. Morris, U. S. P. 1,974,624, Sept. 25, 1934, to Duplate Corp.; *Chem. Abs.*, 1934, 28, 7458.

<sup>c</sup> S. Nishioaka, Japanese P. 100,339, 1933; *Chem. Abs.*, 1934, 28, 2547.

<sup>d</sup> L. Berend, U. S. P. 952,724, Mar. 22, 1910; *Chem. Abs.*, 1910, 4, 1530.

<sup>e</sup> L. Berend, U. S. P. 1,040,850, Oct. 8, 1912; *Chem. Abs.*, 1912, 6, 3534.

<sup>f</sup> Note also K. Albert and L. Berend, French P. 436,720, 1911; *J.S.C.I.*, 1912, 31, 445.

<sup>g</sup> F. G. Wiechmann, U. S. P. 1,089,188, Dec. 2, 1913; *Chem. Abs.*, 1914, 8, 433.

<sup>h</sup> K. I. Tarasov, U. S. P. 1,187,889, June 20, 1916; *Chem. Abs.*, 1916, 10, 2131. British P. 102,751, 1916; *J.S.C.I.*, 1917, 36, 150.

<sup>i</sup> H. Kühl, German P. 280,648, 1913; *Chem. Abs.*, 1915, 9, 1849.

<sup>j</sup> T. Nakanishi, Japanese P. 34,923, 1919; *Chem. Abs.*, 1920, 14, 2270. Cf. Japanese P. 31,921, 1917; *Chem. Abs.*, 1918, 12, 2254.

horn, made from casein) 85 parts and phenol-formaldehyde resin 26 parts. The resin is put into solution before incorporating it with the fillers.<sup>12</sup>

Hagendorf<sup>13</sup> used the serum from the blood of cattle, in conjunction with formic acid and trioxymethylene or formaldehyde. This mixture was heated with phenol and sodium peroxide until a solid product was obtained. Hydrogen peroxide<sup>14</sup> can be substituted for the sodium peroxide and other albumins may take the place of blood serum. In making knobs, buttons or other articles from proteins such as those of blood, casein or yeast, a protein powder is consolidated by the action of a colloidal solution of protein in dichlorohydrin or phenol and formaldehyde.<sup>14a</sup>

Wiechmann<sup>14b</sup> mixed vegetable ivory with phenol and then treated the mixture with formaldehyde, obtaining a thermoplastic substance which could be transformed into a hard, infusible product. The ground vegetable ivory may be mixed with a liquid or pasty form of a partial condensation product of phenol and formaldehyde, and submitted to further heating until on cooling the material is hard enough to be ground. It can now be molded. In another case, ground vegetable ivory is simply mixed with a pulverized solid partial condensation product of phenol and formaldehyde and the composition is molded under heat and pressure to a hard, infusible condensation product. Wiechmann is of the opinion that reaction takes place between the three essential components and that the vegetable ivory actually is in chemical combination in the molded material.

Frood<sup>14c</sup> describes a floor-covering composition. Fibrous material, before or after treatment with a phenol-formaldehyde condensation product, is disintegrated or shredded in such a manner as to preserve the original length of the fibers, and the product is kneaded to a uniform mass with rubber, casein or animal glue, together with filling material and coloring matter. The fibrous material and rubber respectively may be fireproofed by treatment with solutions of sodium silicate, zinc chloride or antimony trichloride or by chlorination. The composition is rolled into sheets or molded into shape and subsequently vulcanized.

Sato investigated various thermoplastic substances made from vegetable proteins (obtained from corn and beans) combined with phenol and formaldehyde.<sup>14d</sup> The protein was incorporated with the phenol and treated with formaldehyde or hexamethylenetetramine. For example, 100 parts by weight of the protein of corn were mixed with 150 parts of phenol and the mass kneaded to produce a thick glue-like transparent substance of light brown color, and 50 parts by weight of trioxymethylene were introduced. Besides using these compositions in making molded articles Sato also made a lacquer by dissolving them in benzene, petroleum benzine or other solvent. He reported that this lacquer hardened at 30-40°C. to a glossy coating which was resistant to water and common organic solvents. Berlin<sup>15</sup> has suggested that corn-gluten residues be utilized to make molded articles. The moldable mix consisted of 100 parts of starch and fat-free gluten, 8 of phenol, 3 of butanol, 2.5 of glycerol, 3 of hexamethylenetetramine, 2.5 of paraformaldehyde and 5 of water. The mixture is heat-hardened by molding at 150°C. and 3000 pounds pressure for 9 minutes. Phosphatides from soya beans or egg yolk can be treated with solvents for the extraction of oils and then mixed with resinous

<sup>12</sup> O. Parkert, Reported by M. Bottler, "Kunstharzen," J. F. Lehmanns Verlag, München, 1919, 63.

<sup>13</sup> K. Hagendorf, German P. 274,179, 1913; *J.S.C.I.*, 1914, 33, 838

<sup>14</sup> K. Hagendorf and A. Breslauer, British P. 17,728, 1914; *Chem. Abs.*, 1916, 10, 259

<sup>14a</sup> H. Plauson, U. S. P. 1,395,729, Nov. 1, 1921; *Chem. Abs.*, 1922, 16, 619

<sup>14b</sup> F. C. Wiechmann, U. S. P. 1,061,346, May 13, 1913; *Chem. Abs.*, 1913, 7, 2319. U. S. P. 1,126,926, Feb. 2, 1915; *Chem. Abs.*, 1915, 9, 872. U. S. P. 1,135,340, Apr. 13, 1915; *Chem. Abs.*, 1915, 9, 1535. U. S. P. 1,218,146, Mar. 6, 1917; *Chem. Abs.*, 1917, 11, 1532.

<sup>14c</sup> H. Frood, British P. 176,405, 1920; *J.S.C.I.*, 1922, 41, 335A.

<sup>14d</sup> S. Sato, U. S. P. 1,245,975, 1,245,976, 1,245,978, 1,245,979, 1,245,980, 1,245,981, 1,245,982, 1,245,983 and 1,245,984, Nov. 6, 1917; *Chem. Abs.*, 1918, 12, 297.

<sup>15</sup> H. Berlin, U. S. P. 1,988,475, Jan. 22, 1935, to Resinox Corp.; *Chem. Abs.*, 1935, 29, 1535.



plastics. The resulting composition is proposed for the manufacture of phonograph records.<sup>16</sup>

Rubber-like compositions can be made by heating animal glues or gelatins with phenols, and adding formaldehyde under energetic mixing. Various varieties of pitch, resins, gums and the like may be incorporated during the mixing.<sup>17</sup> Another rubber substitute which has been described<sup>18</sup> contains strong glue, 100 parts, salicylic acid, 0.2, gum tragacanth, 25, wood flour, 435, water, 200, glycerol, 125, castor oil, 18, colza oil, 11, fatty soap, 6, suet, 3, resinat treated with formaldehyde, 3, solution of resin (Bakelite in naphtha), 5, potassium dichromate, 3, and potassium alum, 6 parts.

A casein-formaldehyde condensation product is treated with phenol and the composition is powdered, placed in molds and hardened under high pressure at a temperature of 100°C. or more.<sup>19</sup> A material of great hardness and toughness, resistant to oils and relatively high temperatures results. Schroder, Jaroslaw and Levis<sup>20</sup> heated alkaline solutions of albuminous substances (casein, blood, intestinal mucin, oils, plasticizers and fillers of various kinds) with phenol and an aldehyde in the presence of ammonia. Pabst<sup>21</sup> used, for example, 460 g. of casein, wet with 90 g. of water and 90 g. of alcohol, and 40 g. of a mixture of phenol, aldol and rosin, to obtain artificial horn. Carpentier<sup>22</sup> poured a solution of casein in 10 per cent sodium carbonate solution into liquid phenol, dissolved sodium salicylate in the mixture and added formaldehyde. After filtration the mixture was heated under reflux, 80 per cent of the water was removed by distillation *in vacuo* and the residue was heated at 100°C. in molds. Waste from the manufacture of albumin-formaldehyde plastic materials may also be dispersed in phenol and treated at a raised temperature with formaldehyde.<sup>23</sup> When phenol-acetone condensation products are modified with casein, horn-like compositions are obtained.<sup>24</sup> To obtain a shellac substitute, Mellanoff<sup>25</sup> added about 4 parts of a casein solution (100 parts of casein in from 400-800 parts of water containing 16 parts of borax and 10 parts of 26 per cent ammonia) to about 5 parts of a condensation product of phenol and formaldehyde. Aqueous dispersions capable of application as paints, binders or adhesives are obtained by incorporating casein, glue or cyclohexanol with a phenol-formaldehyde resin in presence of an emulsifying agent (e.g., triethanolamine or a saponified sulphonated oil).<sup>26</sup>

Carbonel<sup>27</sup> condensed a mono- or polyhydric phenol with formaldehyde or its polymers in the presence of a salt of alginic acid (an albuminous acid from kelp). The condensation products and the alginic acid were precipitated at the same time by a mineral or organic acid. Hotta and Nakajima<sup>28</sup> employed alginic acid in colloidal form, made by boiling sea weed with dilute caustic soda or sodium carbonate, filtering and acidifying with sulphur dioxide. Fifty parts of the acid thus obtained were dissolved in 100 parts of cresol or phenol mixed with 200 parts of 35 per cent formaldehyde and 25 parts of casein, and heated under pressure to produce

<sup>16</sup> F. Frank, U. S. P. 1,977,940, Oct. 23, 1934, to Hanseatische Mühlenwerke A.-G.; *Chem. Abs.*, 1935, 29, 256.

<sup>17</sup> C. Weygang, British P. 111,171, 1917; *Chem. Abs.*, 1918, 12, 544.

<sup>18</sup> L. Laurin and E. Bidot, U. S. P. 1,969,932, Aug. 14, 1934; *Chem. Abs.*, 1934, 28, 6348. French P. 751,798, 1933; *Chem. Abs.*, 1934, 28, 932.

<sup>19</sup> Swiss P. 102,756, 1922, to Soc. industrielle de la Siderolithe, Paris; *Kunststoffe*, 1925, 15, 185.

<sup>20</sup> R. and M. Schroder, E. Jaroslaw and S. Levis, British P. 272,947, 1927, to Jaroslaw's erste Glimmerwaren-Fabr. in Berlin; *Brit. Chem. Abs. B*, 1928, 615. French P. 635,745, 1927; *Chem. Abs.*, 1928, 22, 4740.

<sup>21</sup> F. Pabst, French P. 652,615, 1928; *Chem. Abs.*, 1929, 23, 3588.

<sup>22</sup> P. Carpentier, French P. 620,169, 1926; *Brit. Chem. Abs.*, B, 1928, 826.

<sup>23</sup> German P. 580,134, 1927, to Herold A.-G.; *Chem. Abs.*, 1931, 25, 5305.

<sup>24</sup> R. Greenhalgh, British P. 379,739, 1932, to Imperial Chemical Ind., Ltd.; *Chem. Abs.*, 1933, 27, 4043. French P. 738,156, 1932; *Chem. Abs.*, 1933, 27, 1725.

<sup>25</sup> I. S. Mellanoff, U. S. P. 1,857,691, May 10, 1932, to Kemikal, Inc.; *Chem. Abs.*, 1932, 26, 3944.

<sup>26</sup> H. W. Hutton, French P. 771,933, 1934; *Chem. Abs.*, 1935, 29, 1536. British P. 417,948, 1934; *Chem. Abs.*, 1935, 29, 1537.

<sup>27</sup> A. Carbonel, French P. 711,130, 1930; *Chem. Abs.*, 1932, 26, 1731.

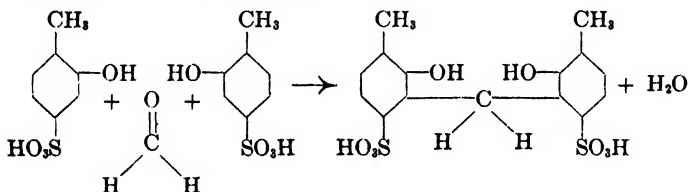
<sup>28</sup> K. Hotta and K. Nakajima, Japanese P. 42,075, 1932, to Nippon Kwaka K. K.; *Chem. Abs.*, 1934, 18, 760.

a resin, soluble in alcohol and amyl acetate. Strong and lustrous films were said to be obtained from it. By combining casein with a phenol-formaldehyde condensation a varnish that may be used for coating bobbins is obtained.<sup>29</sup>

Phenol-formaldehyde resin has been used as a binder for leather scrap. The procedure<sup>30</sup> is to hydrolyze the leather under heat and pressure in the presence of phenol, an aldehyde and an alkaline or acid catalyst. The product is plastic and is useful as a heat- or electrical insulator. Phenol-formaldehyde has also been used as a binder for pulverized natural ivory.<sup>31</sup>

### SULPHONATED DERIVATIVES

Sulphonated phenol-formaldehyde condensation products (syntans) have been utilized for the tanning of skins. These products are reported to be superior to earlier reagents containing phenols. It has long been known that skins may be tanned by means of phenols, and the improvement of utilizing the formaldehyde condensation product had its commercial beginnings sometime previous to 1912.<sup>32</sup> Very likely the use of such products in tanning began in 1909 and was kept as a trade secret.<sup>33</sup> Since that time they have become widely used, especially in conjunction with other tanning materials.<sup>34</sup> In a process described by Stiasny,<sup>35</sup> sulphonated phenol or cresol is added to a 40 per cent solution of formaldehyde, and an exothermic reaction ensues, resulting in the formation of a colorless, viscous mass which is soluble in cold water. The solution can be used as a tanning bath. The reaction involved was considered to be:<sup>36</sup>



These sulphonic acids, and certain of their salts, are absorbed by leather in such a way that they cannot be washed out. They render the leather stable and resistant to tear.<sup>37</sup>

Only one mol of formaldehyde is used to every 2 mols of sulphonated phenol, for the solubility of the product diminishes when the amount of formaldehyde is increased.<sup>38</sup> Paraldehyde may be employed in place of formalin solution, and the resin may be sulphonated after the condensation instead of before.<sup>39</sup> Likewise, acetaldehyde reacts with phenols in the presence of catalytic amounts of sulphuric acid, and the resinous product can be sulphonated to form a tanning substance.<sup>40</sup> The product from

<sup>29</sup> K. Tarasov and G. Zitler, *Izvestiya Tekstil. Prom. Torgov.*, 1931, 10, (12), 55.

<sup>30</sup> R. Collet, French P. 734,335, 1931; *Chem. Abs.*, 1933, 27, 1066.

<sup>31</sup> E. Bormann, U. S. P. 1,885,563, Nov. 1, 1932, to G. Touranchet; *Chem. Abs.*, 1933, 27, 1119. G. Touranchet, German P. 565,846, 1928; *Chem. Abs.*, 1933, 27, 2541.

<sup>32</sup> E. Stiasny, British P. 8511, 1912, to Badische Anilin- & Sodafabrik; *J.S.C.I.*, 1913, 32, 246. *Collegium*, 1913, 142; *J.S.C.I.*, 1913, 32, 500. *J.S.C.I.*, 1913, 32, 775. German P. 262,568, 1911; *J.S.C.I.*, 1913, 32, 878.

<sup>33</sup> C. Blanc, *Bull. soc. ind. Mulhouse*, 1928, 94, 359. L. Meunier, *Ibid.*, 364; *Brit. Chem. Abs. B*, 1928, 828.

<sup>34</sup> A. A. Clafin, *Shoe and Leather Reporter*, 1928, 170 (4), 49; 170 (5), 14.

<sup>35</sup> E. Stiasny, U. S. P. 1,237,405, Aug. 21, 1917, to Badische Anilin- & Sodafabrik; *Chem. Abs.*, 1917, 11, 2125. U. S. P. 1,232,620, July 10, 1917; *Chem. Abs.*, 1917, 11, 2417.

<sup>36</sup> R. B. Croad, *J.S.C.I.*, 1923, 42, 203T.

<sup>37</sup> J. Berkmann, *Collegium*, 1929, 49; *Brit. Chem. Abs. B*, 1929, 405.

<sup>38</sup> L. Meunier and C. Gastellu, *Bull. soc. encour. ind. nat.*, 1927, 126, 732; *Chem. Abs.*, 1928, 22, 1054.

<sup>39</sup> O. Schmidt and A. Andres, U. S. P. 1,254,364, June 22, 1918, to Badische Anilin- & Sodafabrik; *J.S.C.I.*, 1918, 37, 188.

<sup>40</sup> C. J. Herry and A. M. Matheson, U. S. P. 1,695,655, Dec. 18, 1928; *Chem. Abs.*, 1929, 23, 1008.

acetaldehyde is reported to have better filling properties than the corresponding sytan from formaldehyde, but the yield is lower.<sup>41</sup> Higher phenols obtained from peat tar (fraction boiling 240-280°C.) may be sulphonated and then condensed with formaldehyde in alkaline medium. The tannides produced yield a satisfactory leather at a  $pH$  5.5-4.<sup>42</sup> Replacing phenol by resorcinol or pyrogallol also resulted in conferring good filling properties. The tanning action of the naphthol condensation products is comparatively mild.<sup>43</sup> Resorcinol, condensed with benzaldehyde, yields a clear brown syrup, which is a powerful tanning agent.<sup>44</sup> Similarly, phenol alcohols may be condensed with resorcinol.<sup>45</sup> Likewise, tanning agents have been made by incorporating urea resins with polyvalent phenol-formaldehyde condensation products.<sup>46</sup> Crude acetaldehydedisulphonic acid, made from fuming sulphuric acid and acetylene, condenses with phenols in water solution. The product is a soluble tanning agent.<sup>46a</sup>

The sulphonic acid group may be introduced in various ways other than those above noted (sulphonation of the phenol, or the resin). For instance, naphthalene-sulphonic acid is condensed with hydroxybenzyl alcohol;<sup>47</sup> isopropyl-naphthalene-sulphonic acid, with formaldehyde;<sup>48</sup> p-hydroxy-ter-butylbenzenesulphonic acid, with formaldehyde;<sup>49</sup> benzylnaphthalenesulphonic acid, with the phenol-formaldehyde condensation product;<sup>50</sup> alkyl sulphonyl chloride and phenol, with formaldehyde.<sup>51</sup> Hydrogenated syntans can be made by hydrogenating the initial phenol-aldehyde condensation product and introducing the sulphonic group by means of chlorosulphonic acid.<sup>52</sup> Tarasov<sup>53</sup> was able to modify the degree of hardness, elasticity, chemical resistance, solubility and fusibility of the phenol-formaldehyde condensation products by incorporating Russian turpentine oil, sulphonated castor oil (or sunflower seed oil) and sulphonated petroleum. Evidently his products were not intended for use as tanning agents, but were more especially to be used as moldable resins or compositions which could be machined. As an example, a mixture of 50 g. sulphonated sunflower-seed oil, 100 g. phenol, 10 g. sulphonated naphtha and 50 g. formaldehyde is heated. At 50-55°C., an exothermic reaction begins, causing violent ebullition. The mixture becomes viscous, and is poured into molds. Upon further heating it is transformed into a solid free from cracks and bubbles.

Chestakoff,<sup>54</sup> as a means of improving the quality of condensation products from cresol and formaldehyde, proposed the addition of an organic sulphonic acid of high molecular weight and high dispersive power. He employed octahydro-anthracenesulphonic acid, isopropyl-naphthalenesulphonic acid and the acids obtained by sulphonating mineral oils. Polymerized products obtained by the distillation of neutralized sulphonated mineral oil can be incorporated in phenol-formaldehyde resins by heating a mixture of the polymers with phenol and

<sup>41</sup> E. Wolessensky, *Tech. Papers, U. S. Bur. Standards*, 1925, 20, (302), 1; *Brit. Chem. Abs. B*, 1926, 375. See also M. Horn and H. Komori, *Repts. Imp. Ind. Research Inst. Osaka (Japan)*, 1927, 8 (3), 1; *Chem. Abs.*, 1928, 22, 3314.

<sup>42</sup> F. Oспенко and E. Lipkina, *Kozhevenno-Obuvnaya Prom.*, 1934, 13, 473; *Chem. Abs.*, 1934, 29, 2015.

<sup>43</sup> E. Simoncini, *Boll. ufficiale staz. sper. ind. pelli mat. concianti, Suppl. tec.*, 1929, 4, 51, 79; *Chem. Abs.*, 1929, 23, 4366.

<sup>44</sup> H. Noerr, G. Mauthe and A. Doser, U. S. P. 1,908,916, May 16, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3861. *British P.* 331,216, 1925; *Brit. Chem. Abs. B*, 1930, 960.

<sup>45</sup> *British P.* 304,454, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 4844.

<sup>46</sup> F. Pollak, *British P.* 353,872, 1930; *Brit. Chem. Abs. B*, 1931, 1149. See also Chapter 30.

<sup>46a</sup> German P. 383,189, 1921, to Chem. Fabr. vorm. Weiler-ter Meer; *J.S.C.I.*, 1924, 43, 482B.

<sup>47</sup> K. Dachlauer and C. Thomsen, U. S. P. 1,912,260, May 30, 1933; *Chem. Abs.*, 1933, 27, 4043.

<sup>48</sup> I. C. Somerville, U. S. P. 1,722,904, July 30, 1929, to Röhm & Haas Co.; *Chem. Abs.*, 1929, 23, 4593.

<sup>49</sup> *British P.* 388,989, 1932, to Röhm & Haas Co.; *Brit. Chem. Abs. B*, 1933, 482.

<sup>50</sup> K. Dachlauer, C. Thomsen and A. Voss, U. S. P. 1,956,415, Apr. 24, 1934; *Chem. Abs.*, 1934, 28, 4191.

<sup>51</sup> *British P.* 211,145, 1924, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1925, 44, 605.

<sup>52</sup> French P. 757,725, 1921, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1924, 28, 2933.

<sup>53</sup> K. I. Tarasov, U. S. P. 1,216,515 and 1,216,516, Feb. 30, 1917; *Chem. Abs.*, 1917, 11, 127a. U. S. P. 1,235,507, July 31, 1917; *Chem. Abs.*, 1917, 11, 2722. Dutch P. 1,798 and 1,798, 1917; *Chem. Abs.*, 1917, 11, 1278. Russian P. 511 to 514, 1925; *Chem. Abs.*, 1926, 27, 5492. *British P.* 223,636, 1923; *Brit. Chem. Abs. B*, 1925, 16. Russian P. 435, 1925; *Chem. Abs.*, 1926, 27, 4362.

<sup>54</sup> P. Chestakoff, *British P.* 303,023, 1927; *Chem. Abs.*, 1929, 23, 4593.

formaldehyde for 1-6 hours at a temperature of about 100°C., in the presence of a small amount of sulphuric acid.<sup>55</sup> When colophony is heated with phenol and sulphuric acid, clear solutions are formed. That these solutions have good tanning properties is indicated by the fact that they give heavy precipitates with gelatin.<sup>56</sup>

For the preparation of syntans, it occasionally happens that the condensation of phenol with formaldehyde is carried out in the presence of inorganic sulphites. Thus, sulphonated phenol is condensed with formaldehyde in the presence of sulphite, after which oxalic acid is added.<sup>57</sup> Alternatively,<sup>58</sup> the phenol-formaldehyde condensation product can be made first, and then treated with sodium sulphite. The water-soluble products obtained from phenols (phenol, m-cresol, p-chlorophenol) by condensation with formaldehyde and a sulphite are heated with sulphur and water in the presence of alkali, and tanning agents are formed.<sup>59</sup>

The condensation of sulphonated phenol with formaldehyde may be performed in various non-aqueous solvents, acetone, alcohols, ethyl acetate, acetic anhydride and a number of others.<sup>60</sup> In fact, if the tanning materials made in this way are to be used in alcoholic solution, as in the case of skins dehydrated with alcohol,<sup>61</sup> it is not necessary to sulphonate the phenol, or the methylenediphenol condensation product. It is possible to use such a condensing agent as sodium phenolate instead of sulphuric acid. Acetone may be employed before the introduction of the formaldehyde, and thus it also enters into combination with the phenol.<sup>62</sup> The product is made soluble by sulphonation.

In preparing the sulphonated methylenediphenols, acid condensing agents (hydrochloric and sulphuric acids) are usually employed, but many alkaline agents have also been used. Thus, cresol is condensed with formaldehyde in the presence of a small amount of sodium bicarbonate<sup>63</sup> or ammonia,<sup>64</sup> the reaction being carried out in an autoclave at about 110°C. Similarly, sulphonated phenol or cresol condenses with formaldehyde in the presence of ammonia or amines.<sup>65</sup>

The introduction of amido groups into sulphonated phenol-formaldehyde resins evidently improves their tanning properties. Urea, thiourea, polysulphides, calcium thiocyanate and ammonium thiocyanate<sup>66</sup> have been used in this manner. Cyclohexylamine and ammonia may also be employed.<sup>67</sup>

Preliminary condensation of phenol with sulphonated ricinoleic acid, followed by condensation with formaldehyde, has been described as a method for producing tanning agents.<sup>68</sup> An aromatic hydroxy acid, salicylic acid, had been used

<sup>55</sup> F. A. Appgar and A. Runyan, U. S. P. 1,945,719, Feb. 6, 1934, to Sinclair Refining Co.; *Chem. Abs.*, 1934, 28, 2556.

<sup>56</sup> A. Kämpf, German P. 436,445, 1923; *Brit. Chem. Abs. B*, 1927, 421. G. Grasser, *J. Fac. Agric. Hokkaido*, 1929, 24, 73; *Brit. Chem. Abs. B*, 1929, 950. Emulsions of petroleum are also precipitated by sulphonated phenol-formaldehyde resins, according to T. B. Wayne, U. S. P. 1,912,830, May 30, 1933; *Chem. Abs.*, 1933, 27, 4066. For other methods of testing syntans, see J. Berkman, *Vestnik (Organ of the All Russian Leather Syndicate)*, 1928 (3), 211; (6-7), 293; *Collegium*, 1929, 35; *Chem. Abs.*, 1929, 23, 2596. O. Gerngross, *Papier-Fabr.*, 1928, 26, 380; *Chem. Abs.*, 1928, 22, 3800.

<sup>57</sup> French P. 658,874, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 5349. British P. 297,830, 1928; *Brit. Chem. Abs. B*, 1929, 904.

<sup>58</sup> H. Schutte, U. S. P. 1,727,135, Sept. 3, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 5349. E. Kraus, German P. 535,048, 1926, to Fabrik van chem. Producten; *Chem. Abs.*, 1932, 26, 1131. French P. 723,319, 1930, to Progil (Soc. anon.); *Chem. Abs.*, 1932, 26, 4204.

<sup>59</sup> British P. 291,245, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 1304.

<sup>60</sup> G. Grasser, *J. Faculty Agr. Hokkaido Imp. Univ.*, 1929, 24, 73; *Chem. Abs.*, 1929, 23, 3583.

<sup>61</sup> G. Grasser and K. Hirose, *J. Faculty Agr. Hokkaido Imp. Univ.*, 1929, 24, 17; *Chem. Abs.*, 1929, 23, 1785.

<sup>62</sup> W. Moeller, British P. 199,528, 1922; *J.S.C.I.*, 1923, 42, 790A.

<sup>63</sup> R. B. Croad and G. E. Knowles, U. S. P. 1,437,726, Dec. 5, 1922; *Chem. Abs.*, 1923, 17, 897.

<sup>64</sup> R. B. Croad, U. S. P. 1,443,697, Jan. 30, 1923; *Chem. Abs.*, 1923, 17, 1348.

<sup>65</sup> British P. 411,390, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1934, 727.

<sup>66</sup> F. Becherer, U. S. P. 1,982,619, Dec. 4, 1934, to J. R. Geigy A.-G.; *Chem. Abs.*, 1935, 29, 525. British P. 362,797, 1931; *Brit. Chem. Abs. B*, 1932, 198. See also French P. 720,712, 1930, to Progil (Soc. anon.); *Chem. Abs.*, 1932, 26, 4204. French P. 723,319, 1930; *Chem. Abs.*, 1932, 26, 4204.

<sup>67</sup> British P. 221,205, 1924, to Soc. pour l'ind. chim. à Bâle; *Brit. Chem. Abs. B*, 1926, 67.

<sup>68</sup> K. Linder and A. Russe, German P. 569,344, 1927; *Chem. Abs.*, 1933, 27, 2835.

previously in a similar way.<sup>66</sup> It is possible to carry out the condensation between the phenol, formaldehyde and ricinoleic acid, and subsequently sulphonate the resin,<sup>70</sup> or to use oleic acid in place of ricinoleic.<sup>71</sup>

The sulphonation product<sup>72</sup> of a mixture of phenol and a fat, oil, wax or resin can be condensed with an aldehyde to resinous products for use as dispersing and tanning agents. Phenol and wool fat after sulphonation may be condensed with formaldehyde, or cresol and castor oil after sulphonation may be condensed with acetaldehyde.

Other variations from the simple sulphonated methylenediphenols are attained through the introduction of alkyl or substituted alkyl groups, often by means of a condensation reaction in which hydrogen chloride is eliminated. Halogenated phenols may be employed in preparing the initial condensation product,<sup>73</sup> or the ketone or aldehyde to be condensed with the phenol may be chlorinated,<sup>74</sup> as in the case of chloroethyl methyl ketone, chloroacetone, and chloroacetaldehyde. The sulphonated resin from chloroacetone and phenol reacts with waxes, oils and tetrahydronaphthalene, to give products which are still water-soluble.<sup>75</sup> Chlorinated lignite degradation products may be incorporated with phenol-formaldehyde resins, to produce tanning agents.<sup>76</sup> Inorganic catalysts are sometimes of value in assisting the condensation of chlorine compounds with the phenol-formaldehyde product. Thus, p-sulphonylbenzylchloride is condensed in the presence of zinc chloride, aluminum chloride or sodium hydroxide.<sup>77</sup> Instead of the sulphonyl chloride, a mixture of aromatic hydroxy sulphonic acid and sulphur chloride or phosphorus oxychloride may be employed.<sup>78</sup>

Synthetic tanning agents are improved by the addition of fluosilicates,<sup>79</sup> which keep the syntan free from mineral acid. For example, cresolsulphonic acid is condensed with formaldehyde, and the product is neutralized with sodium carbonate. Then, dry sodium fluosilicate is added until the amount present is one-third of the weight of the product.

Still another modification of the sulphonated phenol-formaldehyde resins is the combination of the initial condensation product with sugars or cellulose derivatives, especially waste sulphite cellulose liquor.<sup>80</sup> Grape sugar, fruit sugar, levulinic acid and salicylaldehyde have also been used.<sup>81</sup> A specific procedure is: 100 parts of dextrose are dissolved in 350 parts of sulphuric acid, and 150 parts of phenol are added at a temperature of 40°C. while the mixture is kept agitated. The resulting product is neutralized with caustic soda.<sup>82</sup> The affinity which exists between cellulose derivatives and compositions of the syntan type is made use of by employing these com-

<sup>66</sup> A. Koetzle, U. S. P. 1,344,950, June 29, 1920, to Rohm & Haas Co.; *Chem. Abs.*, 1920, 14, 2565.

<sup>70</sup> British P. 356,105, 1930, to Röhm & Haas Co.; *Chem. Abs.*, 1932, 26, 4426. German P. 543,431, 1930; *Chem. Abs.*, 1932, 26, 2561.

<sup>71</sup> I. C. Somerville, U. S. P. 1,924,052, Aug. 22, 1933, to Rohm & Haas Co.; *Chem. Abs.*, 1933, 27, 5574. Canadian P. 311,566, 1931; *Chem. Abs.*, 1931, 25, 3448. French P. 697,327, 1930; *Chem. Abs.*, 1931, 25, 2875.

<sup>72</sup> French P. 732,931, 1932, to J. R. Geigy A.-G.; *Chem. Abs.*, 1933, 27, 381. British P. 388,936, 1932; *Brit. Chem. Abs.* B, 1933, 399. British P. 330,252, 1931, to Établ. Kuhlmann; *Brit. Chem. Abs.* B, 1932, 1114. French P. 734,318, 1931.

<sup>73</sup> French P. 695,602, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2822.

<sup>74</sup> K. Dachlauer and C. Thomsen, U. S. P. 1,732,503, Oct. 22, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 262. British P. 248,782, 1925; *Chem. Abs.*, 1927, 21, 805.

<sup>75</sup> British P. 302,666 and 302,988, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 241.

<sup>76</sup> British P. 332,204 and 332,270, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 960.

<sup>77</sup> G. Kränzlein and A. Voss, U. S. P. 1,825,802, Oct. 6, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 621. German P. 408,871, 1923; *J.S.C.I.*, 1925, 44, 414B. A. Voss, German P. 456,951, 1923; *Brit. Chem. Abs.* B, 1930, 340.

<sup>78</sup> O. L. Beer, French P. 738,167, 1932; *Chem. Abs.*, 1933, 27, 1782.

<sup>79</sup> J. Schäfer, U. S. P. 1,706,325, Mar. 19, 1929, to J. R. Geigy A.-G.; *Chem. Abs.*, 1929, 23, 2320. British P. 276,014, 1926; *Chem. Abs.*, 1928, 22, 2488. Swiss P. 130,434, 1927; *Chem. Abs.*, 1929, 23, 3126. French P. 639,097, 1927; *Chem. Abs.*, 1929, 23, 730.

<sup>80</sup> V. Casaburi, *Boll. ufficiale staz. sper. ind. pell. mat. concianti*, 1927, 5, 377; *Chem. Abs.*, 1928, 22, 3800.

<sup>81</sup> British P. 189,190, 1921, to Badische Anilin- & Sodafabrik; *Chem. Abs.*, 1924, 18, 766.

<sup>82</sup> S. Kohn, U. S. P. 1,460,422, July 3, 1923, to Röhm & Haas Co.; *Chem. Abs.*, 1923, 17, 2974.

positions in dispersing insoluble dyes for acetate rayon.<sup>55</sup> The staining of esterified-cellulose threads is diminished by adding to the dyebath condensation products of aromatic phenols with sulphuric acid and formaldehyde.<sup>56</sup>

The sulphonated methylenediphenols have the power of colloiddally retaining gases, and have been used as "foaming agents."<sup>57</sup> Another group of sulphonated phenol-formaldehyde resins is constituted by the products which result from treating the initial resin with substituted sulphonyl chlorides. These resins are characterized by a comparatively light color, which is fairly stable in the presence of light and air. Melamid<sup>58</sup> obtained resin-like substances by condensing a phenol and formaldehyde to produce a phenol-alcohol, and subsequently esterifying in caustic soda solution with a benzol solution of an aromatic sulphonyl chloride. For example, 100 kg. of cresol-alcohol (made from commercial cresol and formaldehyde) are dissolved in 300 kg. of 10 per cent caustic soda solution and the solution stirred for several hours at a temperature not exceeding 30°C. with 137 kg. of a mixture of o- and p-toluene sulphonyl chloride or one or other of these isomers in 500 kg. of benzene. The benzene is washed free from alkali, dried, and the resin recovered by evaporation. The initial phenol-alcohol may be made in the presence of the aromatic sulphonyl chloride and the product further treated with sulphonyl chloride. Phosgene or an organic acid anhydride, e.g., acetic anhydride, may be used instead of the sulphonyl chlorides.

Melamid's observations, according to Jacobsohn,<sup>59</sup> resulted in the development of a light-yellow, odorless resin of notable stability of color. A soluble resin of low melting point first is prepared from cresol and formalin, using a small proportion of hydrochloric acid as a catalyst. The resin is esterified with p-toluenesulphonyl chloride, or it may be acetylated. The protection given the hydroxyl groups by this treatment improves the color stability of the resin. Resins treated with p-toluenesulphonyl chloride harden rapidly in the cold.<sup>60</sup>

Phenols treated with sodium bisulphate and thiosulphate can be converted, according to Pfautsch,<sup>61</sup> into synthetic resins which do not discolor on keeping.

Bucherer<sup>62</sup> recommended that the free phenolic groups of the resinous condensation products from phenols and formaldehyde be substituted by organic radicals (alkyl, aralkyl or acyl groups) to render the products insoluble in alkali, and to modify their solubility in organic solvents. p-Toluenesulphonic, benzoic, salicylic, cinnamic, acetic, valeric and bromovaleric esters of the resins, their benzyl ethers and mixed ether-esters are soluble in various organic solvents. Their carbonic acid esters, which are practically insoluble and have high melting points, may be prepared *in situ* upon textiles, wood, paper, by treating the material impregnated with alkaline solutions of the resins with carbonyl chloride.

In the manufacture of colorless<sup>63</sup> or very light-colored insoluble condensation products from phenols and aldehydes, the color-forming constituents of the readily condensable intermediate products are removed by extraction with such agents as ether.

<sup>55</sup> C. S. Bedford, British P. 399,533, 1933; *Brit. Chem. Abs.* B, 1933, 1053.

<sup>56</sup> British P. 306,876, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1929, 430.

<sup>57</sup> C. Hollins and E. Chapman, British P. 280,302, 1926, to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1928, 22, 3003. E. Chapman, British P. 289,630, 1927, to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1929, 23, 681.

<sup>58</sup> M. Melamid, U. S. P. 1,648,858, Nov. 8, 1927; *Chem. Abs.*, 1928, 22, 505. British P. 137,291, 137,292 and 137,293, 1919; *J.S.C.I.*, 1921, 40, 520A. British P. 143,185 and 143,187, 1920, addn. to 132,291; *Chem. Abs.*, 1920, 14, 2865. British P. 133,712 and 133,713, 1919; *Chem. Abs.*, 1920, 14, 852.

<sup>59</sup> M. Jacobson, *Kunststoffe*, 1921, 11, 105; *Chem. Abs.*, 1922, 16, 1202. See also O. Beyer, *Chem.-Ztg.*, 1921, 40, 459.

<sup>60</sup> K. Dietz, K. Frank and E. Thiel, German P. 506,409, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 4616.

<sup>61</sup> M. Pfautsch, German P. 341,231, 1919; *J.S.C.I.*, 1922, 41, 93A.

<sup>62</sup> H. Bucherer, U. S. P. 1,697,718, Jan. 1, 1929; *Chem. Abs.*, 1929, 23, 1294. British P. 148,189, 1920; *Chem. Abs.*, 1921, 15, 183. British P. 148,866, 1920; *Chem. Abs.*, 1921, 15, 319.

<sup>63</sup> German P. 233,395, 1910, to Bakelite G.m.b.H.; *Chem. Abs.*, 1911, 5, 2745.

## CHLORINATED COMPOUNDS AS SOFTENING AGENTS

Just as formaldehyde or hexamethylenetetramine increases the rate of conversion of fusible, soluble, soft resin into infusible insoluble hardened resin, so also many substances, called softening agents, tend to prevent the progress of this conversion or to soften the product, once the conversion has taken place. Monochloronaphthalene is especially useful for this purpose. It is liquid at room temperature, and remains in the hardened composition, evidently dissolved in the solid resin.<sup>92</sup> Instead of monochloronaphthalene, other chlorinated compounds, tetra- or pentachlorophenol, may be employed.<sup>93</sup>

A resin was made by Mannesmann<sup>91</sup> from phenols, especially m-cresol, and aldehydes in the presence of chlorinated hydrocarbons, and without acid or alkaline catalysts.

Cresol-formaldehyde resin is soluble in monochloronaphthalene in all proportions. Phenol-formaldehyde resin and monochloronaphthalene, however, are not mutually soluble in all proportions. Monochloronaphthalene is soluble in an equal amount of phenol resin when heated, but larger amounts of monochloronaphthalene will not remain in solution.

Enamel or lacquer compositions which are to be hardened by subsequent heat treatment may be made by compounding cresol-resin and hexamethylenetetramine with free cresol and a fluid chloronaphthalene. The proportions of the latter ingredient may vary within wide limits, as much as 2 parts of the monochloro compounds to 1 part of the cresol resin being used, the amount depending on the fluidity and character desired in the varnish or lacquer. Free cresol may also be added and if employed in large percentages, the amount of hexa is proportionally increased.

Free cresol is used, if monochloronaphthalene is the solvent, for thinning the composition and also because it yields a better impregnating varnish, for coils and the like. In such a composition, the hardening agent (hexamethylenetetramine or trioxymethylene or some other solid anhydrous polymer of formaldehyde) is added in the proportion of 3 or 4 per cent of the weight of the cresol resin plus 20-25 per cent of the weight of the free cresol used. Also, solid chloronaphthalenes or chlorophenols may be added to the solution since they have the property of reducing the shrinkage of the varnish film during and after hardening, the coefficient of expansion of the cresolic compositions being greater than that of resins made from phenol.<sup>96</sup>

Aylsworth utilized a combination of chloronaphthalene and phenylphthalimide, in these proportions: 100 parts phenol resin, 10-30 parts cresol or monochloronaphthalene, 20-70 parts phenylphthalimide, 0-100 parts filler.<sup>95</sup> Baekeland employed a chlorinated hydrocarbon with anhydroformaldehyde-aniline. Sym.-dichloroethane, tetrachloroethane and monochloronaphthalene were the chlorine compounds specified.<sup>97</sup> Likewise, Petrov<sup>98</sup> employed the chlorinated derivatives of ethane and ethylene, combining these in the presence of either acid or alkaline catalysts, with the semi-condensed products of phenol-formaldehyde.

<sup>92</sup> J. W. Aylsworth, U. S. P. 1,090,439, Mar. 17, 1914, to Condensite Co. of America; *Chem. Abs.*, 1914, 8, 1690.

<sup>93</sup> J. W. Aylsworth, U. S. P. 1,046,137, Dec. 3, 1912; *Chem. Abs.*, 1913, 7, 712.

<sup>94</sup> R. Mannesmann, Danish P. 24,697, 1919; *Chem. Abs.*, 1920, 14, 1227.

<sup>95</sup> J. W. Aylsworth, U. S. P. 1,087,422, Feb. 17, 1914; *Chem. Abs.*, 1914, 8, 1354. Reissues 14,530 and 14,531, Oct. 18, 1918; *Chem. Abs.*, 1919, 13, 80. L. V. Redman, A. J. Weith and F. P. Brock (U. S. P. 1,242,563, Oct. 9, 1917; *Chem. Abs.*, 1918, 12, 209) also used naphthalene, anthracene, creosote oils and camphor as plasticizing agents. G. S. Weith, U. S. P. 1,975,884, Oct. 9, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 7553.

<sup>96</sup> J. W. Aylsworth, U. S. P. 1,102,633, July 7, 1914; *Chem. Abs.*, 1914, 8, 3127.

<sup>97</sup> L. H. Baekeland, U. S. P. 1,216,265 and 1,216,266, Feb. 20, 1917; *Chem. Abs.*, 1917, 11, 1279. U. S. P. 1,217,115, Feb. 20, 1917; *Chem. Abs.*, 1917, 11, 1279.

<sup>98</sup> G. S. Petrov, Russian P. 4333, 1923; *Chem. Abs.*, 1929, 23, 1227.

Polychlorinated naphthalene also finds application in conjunction with phenol-formaldehyde resins. Benzoic acid, which may also be used for controlling the polymerization of the intermediate resins, is not superior to polychlorinated naphthalene or many other cheap waxy materials.<sup>99</sup> A mixture of 14 parts Halowax (chlorinated naphthalene), 16 parts 45 per cent phenol-formaldehyde resin solution, 2 parts aluminum stearate and 13 parts maize oil is applied to a fabric backing to make a stencil paper.<sup>100</sup> The resin is heat-hardened on the sheet. Sealing compositions can be made by dissolving a phenolic resinoid in wax-like halogenated naphthalene.<sup>101</sup>

Guntzel proposed a method for producing a viscous phenol condensation product containing p-dichlorobenzene. One l. of phenol is mixed with 600 cc. 40 per cent formaldehyde solution. About 80 g. p-dichlorobenzene is introduced, and the mixture is heated to melt the dichlorobenzene, and, under vigorous stirring, to form a homogeneous mixture. A mixed salt consisting of 60 parts common salt, 10 parts ammonium chloride and 30 parts hexamethylenetetramine is then added in quantity corresponding to one per cent of the weight of phenol used. After the batch has been heated for a time, it is washed several times with cold water. The liquid syrupy product which remains may be hardened by heat.<sup>102</sup>

Weith<sup>103</sup> described the preparation of a resin by the use of a rather large amount of hexamethylenetetramine in the initial stage together with a plasticizing agent. Equimolar portions of methylene and phenol would require 6 mols of phenol to 1 of hexamethylenetetramine, but Weith employed a proportion of 3 to 1. In his procedure, 175-190 g. phenol, 25-10 g. o-cresol, 86 g. hexamethylenetetramine and 65 g. monochloronaphthalene are mixed together. To this is added 2 cc. butyl stearate and 1.5 cc. castor oil. The mixture is heated in an open vessel to 135°C., at which temperature an exothermic reaction begins. When the reaction has become slower, and the temperature has fallen to 125°C., the mass is poured into shallow molds, in which it is hardened at 120°C. under 80 pounds pressure.

#### AMINES AS SOFTENING AGENTS

Bakeland used aniline as a solvent or flux for infusible phenol-formaldehyde resins.<sup>104</sup> Aniline has a pronounced softening action on these resins, especially at high temperatures, and permits infusible particles or fragments to be welded together into compact, coherent masses under heat and pressure. A variety of amines, including xylidines, toluidines, benzidine and diphenylamine, has been proposed<sup>104a</sup> for use with phenol-hexamethylenetetramine resins. According to Hubacher,<sup>106</sup> the resin made from acetaldehyde and phenol modified with aniline may be employed as an antioxidant in vulcanized rubber. The introduction of aniline into a phenol-formaldehyde resin may be carried out<sup>106</sup> by first condensing the amine with formaldehyde in the presence of water at room temperature, and then mixing the product with an alkaline solution of phenol-aldehyde resin in a water-miscible solvent (alcohol). A composite easily moldable product precipitates.

The condensation product of aniline and formaldehyde is anhydroformaldehydeaniline,  $(\text{CH}_2\text{NC}_6\text{H}_5)_3$ , and this may be used in place of aniline as a softening agent. Goldsmith obtained a compound soluble in acetone and having the physical characteristics of a resin by heating together a phenol or a fusible phenol-

<sup>99</sup> German P. 384,147, 1920, addn to 351,104, to Wenjact G.m.b.H.; *J.S.C.I.*, 1924, 43, 527.

<sup>100</sup> K. W. Carr, U. S. P. 1,916,203, July 4, 1933, to Ditto, Inc.; *Chem. Abs.*, 1933, 27, 4641.

<sup>101</sup> E. R. Hanson and M. E. Delaney, U. S. P. 1,865,629, July 5, 1932, to Halowax Corp.; *Brit. Chem. Abs. B*, 1933, 399.

<sup>102</sup> R. Guntzel, U. S. P. 1,711,411, Apr. 30, 1929, to Schieferweike Ausdauer A.-G.; *Chem. Abs.*, 1929, 23, 3060. French P. 650,512, 1928; *Chem. Abs.*, 1929, 23, 3285. German P. 529,323, 1927; *Chem. Abs.*, 1931, 25, 5050. French P. 650,442, 1928; *Chem. Abs.*, 1929, 23, 3285. British P. 236,731, 1927; *Chem. Abs.*, 1929, 23, 533.

<sup>103</sup> G. S. Weith, U. S. P. 1,975,884, Oct. 9, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 7563.

<sup>104</sup> L. H. Bakeland, U. S. P. 1,133,083, Mar. 23, 1915; *Chem. Abs.*, 1915, 9, 1227.

<sup>104a</sup> British P. 363,694, 1930, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 1774.

<sup>106</sup> M. H. Hubacher, U. S. P. 1,848,721, Aug. 3, 1932, to Rubber Service Laboratories; *Brit. Chem. Abs. B*, 1933, 33.

<sup>106</sup> P. F. Schlingman and R. H. Kienle, British P. 400,698, 1933, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1934, 28, 2137.



formaldehyde resin and anhydroformaldehydeaniline.<sup>107</sup> It might be expected that the methylene groups which it contains would cause a hardening action, and, in fact, Baekeland<sup>108</sup> found that the use of up to 110-130 parts of anhydroformaldehydeaniline to 100 parts of fusible resin is accompanied by increase in the hardness of the final product, while still higher proportions show increased plasticity, especially at high temperatures. This reagent, in contrast with hexamethylenetetramine, liberates no readily volatile by-product in the hardening of a resin from a fusible to an infusible state. Baekeland incorporated the anhydroformaldehydeaniline through the use of a hydrocarbon solvent.

Bender<sup>109</sup> prepared resins by condensing phenol with anhydroformaldehydeaniline, following up with hexamethylenetetramine and fillers. He subscribed<sup>110</sup> to the theory that when aniline is used as a condensing agent<sup>111</sup> in the preparation of phenol-formaldehyde resins, anhydroformaldehydeaniline is first formed, and that this body reacts with a portion of the phenol, setting free aniline, thus providing for a recurrence of the cycle. He therefore considers reactions involving anhydroformaldehydeaniline to be substantially similar to those occurring when aniline and formaldehyde are introduced separately.

Thus, 250 parts of aniline are added to a mixture of 500 parts phenol, 800 parts 37.5 per cent formaldehyde and 5 parts hexamethylenetetramine. At first, considerable heat is evolved, and then the reaction requires heating to keep the mixture at 160°C. until free from water. Upon sufficient application of heat a hard, infusible body is formed. Products of this type have excellent electrical insulating properties. Lume may be used instead of hexamethylenetetramine in the initial condensation, and aniline may be expelled from the condensation product by distillation under reduced pressure.<sup>112</sup>

Resins which are thermohardening, light-resistant and soluble in common low-boiling solvents are formed when formaldehyde is caused to react with phenol, urea and p-toluenesulphonamide.<sup>113</sup> In a similar procedure, Bender<sup>114</sup> caused phenol to react with formaldehyde, combining the excess formaldehyde with urea, thiourea or p-toluenesulphonamide. After acidification, the mass was dissolved in alcohol to form a varnish.

Modification of phenol-formaldehyde resins can be brought about by the use of fatty acids and amines. For example, 56.8 parts by weight of stearic acid and 18.6 parts of aniline are heated at 170-200°C., allowing the water formed to escape. After 1 hour, 19 parts of furfural are added, and the whole mass is heated to about 200°C for approximately 0.5 hour. On cooling, it solidifies to a dark brown waxy solid which may be added to phenolic condensation products to promote ease of molding.<sup>115</sup>

According to Groff<sup>116</sup> it has been commonly considered that molded articles containing considerable proportions of nitrogen are apt to be deficient in electrical insulating quality, but this rule does not apply if the molded product is substantially dehydrated and sufficiently impervious to water. The addition of rosin or carnauba wax and mica to a phenol-hexamethylenetetramine resin increases the water-repelling character, and also results in retarding the conversion of the fusible resin to the infusible form.

Assisting-agents for use in dyeing may be made by causing organic nitrogen bases (e.g., aniline, diethylamine, pyridine) to react with the condensation product

<sup>107</sup> G. B. Goldsmith, U. S. P. 1,168,626, Jan. 18, 1916; *Chem. Abs.*, 1916, 10, 826. U. S. P. 1,188,439, June 27, 1916; *Chem. Abs.*, 1916, 10, 2157. U. S. P. 1,228,428, June 5, 1917; *Chem. Abs.*, 1917, 11, 2283. U. S. P. 1,230,829, June 19, 1917; *Chem. Abs.*, 1917, 11, 2283. See also Chapter 33.

<sup>108</sup> L. H. Baekeland, U. S. P. 1,216,265, Feb. 20, 1917; *Chem. Abs.*, 1917, 11, 1279.

<sup>109</sup> H. L. Bender, British P. 280,521, 1926, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 3308.

<sup>110</sup> H. L. Bender, U. S. P. 1,955,731, Apr. 24, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 4256. British P. 280,521, 1927; *Brit. Chem. Abs. B*, 1929, 294.

<sup>111</sup> L. H. Baekeland, U. S. P. 942,809, Dec. 7, 1909; *Chem. Abs.*, 1910, 4, 680. L. Helm, British P. 25,216, 1907; *J.S.C.I.*, 1908, 27, 412.

<sup>112</sup> H. L. Bender, British P. 304,659, 1926, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 4837.

<sup>113</sup> A. Sptzer, British P. 409,490, 1933; *Brit. Chem. Abs. B*, 1934, 591.

<sup>114</sup> H. L. Bender, U. S. P. 1,650,109, Nov. 22, 1927, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 505. British P. 280,250, 1926; *Chem. Abs.*, 1928, 22, 3308.

<sup>115</sup> O. A. Cherry and F. Kurath, U. S. P. 1,896,069, Feb. 7, 1933, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1933, 27, 2541.

<sup>116</sup> F. Groff, U. S. P. 1,931,958, Oct. 24, 1933, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 663.

prepared by adding phenol to a hydrochloric acid-formaldehyde solution.<sup>117</sup> A solution for coating or impregnating paper can be made by modifying a phenol resin with natural resins. The procedure<sup>118</sup> is to react formaldehyde with a mixture of  $\beta$ -naphthol and phenol or resorcinol, and to add shellac, rosin, sandarac and kerosene or benzene. Sodium sulphite is now introduced, and the mixture is warmed to 80-85°C. After cooling, milk of lime solution, or an aqueous solution of coloring substances, is added. The impregnation takes place at 180-200°C. under pressure.

#### RESINS MODIFIED BY WAXES, PITCH, GUMS, OR TARs

Tar oils, tars and pitches may be blended with reactive phenol-formaldehyde resins by first reacting the tarry matter with sulphur chloride or thionyl chloride, and then melting the factice with the phenol-formaldehyde condensation product.<sup>119</sup> Sulphonated resins, subsequently treated with ammonia or an organic base, will combine with various gums and waxes.<sup>120</sup> Also, sulphonated fats and waxes (wool fat, carnauba, spermaceti) can be treated with formaldehyde, and then condensed with phenol.<sup>121</sup> Saponifiable waxes such as montan wax, beeswax or carnauba wax may be united with phenol-formaldehyde resins by esterifying the carboxyl groups of the waxy acids with the hydroxyl groups of the resin. The products are thermoplastic, but they do not melt. If formaldehyde is added during the esterification, the resulting resin is hard and not thermoplastic.<sup>122</sup>

Nash used stearin pitch as a modifier<sup>123</sup> by dissolving it in benzene. After adding 5 parts of the solvent to 15 parts of the pitch, the solution is mixed with approximately 142 parts by weight of phenolic condensation product, and the mixture is kneaded with 500 parts of asbestos or other filler to yield a material which can be molded and cured by heat-treatment. Because of the plasticity imparted by the stearin pitch, the resin may be worked in a more advanced stage of condensation. Novotny<sup>124</sup> proposed to modify synthetic resins by adding natural resins of plant origin containing phenolic tannols (red and yellow gum accroides, gum benzoin and dragon's blood). As an example, 50 parts by weight of U. S. P. phenol, 42.5 parts of furfural and 35 parts of gum accroides are mixed together, and heated to dissolve the gum. The mixture is strained to remove impurities, and 0.75 parts of potassium carbonate are added to the clear product. After refluxing or preferably distilling through a separator (see Chapter 17) for 2.5 hours, an end temperature of 200°C. is reached and a hard grindable resin melting at approximately 200°C. is produced.

A plasticized composition for coating and lining pipes that are subjected to low temperatures is prepared by incorporating a mixture of pitch and asphalt with a phenol-formaldehyde condensation product at 230°C.<sup>125</sup> A non-inflammable composition to be utilized as a polish for wood or leather contains chloronaphthalene, a phenol or cresol resin and carbon tetrachloride.<sup>126</sup> Waxy materials were also used by Pungs and Stade,<sup>127</sup> who condensed phenol and formaldehyde with an alkaline condensing agent in an emulsion of wax such as carnauba, montan or beeswax. The

<sup>117</sup> A. Brunner, German P. 551,872, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4965.  
German P. 550,826, 1929; *Chem. Abs.*, 1932, 26, 4065

<sup>118</sup> British P. 308,560, 1929, to Worldecho, Ltd.; *Chem. Abs.*, 1930, 24, 253.

<sup>119</sup> G. Baile and K. Daimler, German P. 475,478, 1922, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 3360.

<sup>120</sup> British P. 221,205, 1923, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1925, 19, 902.

<sup>121</sup> French P. 734,318, 1931, to Établ. Kuhlmann; *Chem. Abs.*, 1933, 27, 1116.

<sup>122</sup> British P. 327,713 and 327,417, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5118.

<sup>123</sup> C. A. Nash, U. S. P. 1,574,842, Mar. 2, 1926, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1926, 20, 1530.

<sup>124</sup> E. E. Novotny, U. S. P. 1,902,461, Mar. 21, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3351.

<sup>125</sup> F. C. Langenberg, H. S. Hunt and H. G. Reddick, U. S. P. 1,911,131, May 23, 1933, to U. S. Pipe & Foundry Co.; *Chem. Abs.*, 1933, 27, 4054.

<sup>126</sup> J. W. Aylsworth, U. S. P. 1,090,440, Mar. 17, 1914, to Halogen Products Co.; *Chem. Abs.*, 1914, 18, 1647.

<sup>127</sup> W. Pungs and W. Stade, German P. 556,895, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5778. German P. 540,361, 1928; *Chem. Abs.*, 1932, 26, 1313. German P. 543,612, 1928; *Chem. Abs.*, 1932, 26, 3392.

waxes may be replaced by the wax acids or their salts. Hónel<sup>128</sup> used other phenolic resins for the same purpose. In the preparation of these resins p-cresol, p-amyl phenol or p-butyl phenol replaced phenol.

Plastic masses, stated to be useful as insulating material, were obtained by Plauson<sup>129</sup> by modifying phenol-aldehyde resins with lignite-extracts. Powdered lignite is treated with caustic soda, the extract filtered and treated with a concentrated mineral acid and evaporated to dryness. The residue is added to a mixture of a ketone or aldehyde (for example, acetone or formaldehyde), a phenol (e.g., resorcinol) and concentrated hydrochloric acid and the whole is heated under pressure at 150-200°C. A homogeneous black mass results.

### THE USE OF CHLOROACETIC ACID

It is evident that, if a carboxyl group is present in a synthetic resin the possibility of esterification with hydroxyl groups is introduced. In this way the properties of the resin can be considerably altered. Accordingly, when partly condensed aldehyde-phenol products are heated with chloroacetic acid or  $\beta$ -bromopropionic acid in the presence of alkali, fusible carboxylated resins which are soluble in alkali are obtained.<sup>130</sup> The haloaliphatic acid may be introduced after the resin has been prepared, in which case less than 1 mol of halogen fatty acid is used.<sup>141</sup> Dichloroacetic acid, or chloromalonic acid may be used in like manner.<sup>132</sup>

The ammonium salt (or substituted ammonium salt) of carboxylated phenol-formaldehyde resin has valuable properties. It is soluble in water and various kinds of fillers may be added to its aqueous solution. With paper pulp it forms a resin which can be used in the manufacture of molded articles. With glycol, glycerol, mannitol or polyvinyl alcohol (obtained by the saponification of polyvinyl acetate),<sup>133</sup> it forms an insoluble, infusible body.<sup>134</sup>

It is not essential to use the ammonium salt when the carboxylated resin is to be reacted with polyhydric alcohols. The carboxy derivative may be precipitated by acid and then esterified with glycol or glycerol. The product is insoluble and infusible, but remains elastic when heated to 150-170°C.<sup>135</sup> A phenoxy aliphatic acid may be substituted for chloroacetic.<sup>136</sup>

A further modification of the polyhydric-alcohol-esterified-carboxylated phenol-formaldehyde resin is attained through the addition of linseed oil fatty acids or ricinoleic acid.<sup>137</sup> The product is a water-resistant binding agent for abrasants.

### POLYHYDRIC ALCOHOLS

The addition of glycerol as a softening or plasticizing agent to phenol-aldehyde resins has received much attention. Purified phenol-aldehyde resins (prepared by washing the crude condensates with hot water, dilute acid and cold water) are

<sup>128</sup> H. Hónel, U. S. P. 1,996,070, Apr. 2, 1935, to Beck, Koller & Co.

<sup>129</sup> H. Plauson, German P. 376,743, 1914; *J.S.C.I.*, 1924, 43, 641B.

<sup>130</sup> German P. 439,962, 1920, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1927, 822. German P. 364,040, 1919; *J.S.C.I.*, 1923, 42, 613A.

<sup>131</sup> German P. 386,733, 1920, to Farb. v. Meister, Lucius & Brünig; *J.S.C.I.*, 1934, 43, 604B. German P. 391,539, 1920; *J.S.C.I.*, 1924, 43, 840B.

<sup>132</sup> German P. 449,276, 1920, addn. to 386,733, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1928, 866.

<sup>133</sup> See also Chapters 51 and 46.

<sup>134</sup> A. Voss, U. S. P. 1,892,227, Dec. 27, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2001. U. S. P. 1,860,441, May 31, 1932; *Chem. Abs.*, 1932, 26, 3885. German P. 470,870, 1927; *Chem. Abs.*, 1929, 23, 2309. German P. 553,073, 1929; *Chem. Abs.*, 1932, 26, 6166. British P. 298,085, 1928; *Brit. Chem. Abs. B*, 1930, 520. French P. 661,059, 1928; *Chem. Abs.*, 1930, 24, 212. W. Kacykowski and H. Piotnik, French P. 744,182, 1933; *Chem. Abs.*, 1933, 27, 4042.

<sup>135</sup> A. Voss, U. S. P. 1,805,883, May 12, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3855. German P. 473,171, 1927; *Chem. Abs.*, 1929, 23, 8115.

<sup>136</sup> British P. 326,214, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 4175.

<sup>137</sup> British P. 376,121, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 902.

believed to combine with the polyhydric alcohols,<sup>138</sup> the amount of combination being probably dependent on the amount of free phenol or aldehyde present in the resin. Simple plasticization is not accompanied by chemical combination.

In the presence of catalysts (sulphuric and sulphurous acids and salts) and upon prolonged refluxing, glycerol resinifies to form a dark-brown, viscous, water-soluble product. On further heating, loss of water occurs, and the resin becomes infusible. The initial resin corresponds to the formula  $(C_7H_5O_2)_n$ , and apparently contains 2 hydroxyl groups. It is suggested as an adjuvant to bakelite-type materials.<sup>139</sup> Instead of resinified glycerol, a resinous mixture<sup>140</sup> containing a glycerol-polycarboxylic condensation product and natural resin may be used, sufficient glycerol being provided to esterify the acid groups of the natural resin. A similar procedure is to condense the phenol-formaldehyde resin with a carboxylic acid (oxalic, succinic, lactic), introducing the polyhydric alcohol (glycerol, glycol, polyglycerols) during the last stages of the condensation.<sup>141</sup> Still another variation is to heat the phenol-formaldehyde resin with a fatty acid glyceride (castor oil, boiled linseed oil) in the presence of a monohydric alcohol, which can to a certain extent liberate glycerol from the glyceryl ester.<sup>142</sup> If the initial synthetic resin is so constituted that it contains a carboxyl group, it can be modified by heating first with a fatty acid or fatty acid ester of low volatility, and subsequently with a polyhydric alcohol, preferably in a vacuum at 150-200°C.<sup>143</sup>

Beckmann and Dehn have been able to modify the phenol-furfural resins by means of a wide variety of agents, including polyhydric alcohols.<sup>144</sup> Luft<sup>145</sup> and Lebach<sup>146</sup> suggested the use of substances such as camphor, rubber and glycerol to prevent hardening of phenol-aldehyde resins. A similar use of glycerol was proposed by Grognot.<sup>147</sup> Labbé<sup>148</sup> added acetone or glycerol to produce transparent phenol resins.

Mehta<sup>149</sup> heated phenols or cresols with an equimolecular proportion of formaldehyde in the presence of potassium or sodium hydroxide and a small proportion of ammonia and glycerol *in vacuo* at 100-125°C. for 6 hours. Typical proportions are 65 parts of phenol, a corresponding equimolecular quantity of formaldehyde, 0.1063 part of potassium hydroxide, 1 part of ammonia and from 2-10 per cent of the weight of the mixture of glycerol. The only liquid thus obtained is hardened by heating in a mold *in vacuo* for 1 hour and then at 0.5 atmosphere pressure for 2 hours at 150°C. These resins are stated to be specially resistant to decolorizing by sunlight. The function of the glycerol appears to be to take care of the small amounts of water that are not removed by the vacuum-hardening. If less than 1 per cent of glycerol is used the product is opaque, with more than 10 per cent it is hygroscopic. Without ammonia, the resin is clear and with ammonia it resembles amber.

Schmidt<sup>150</sup> added polyhydric alcohols or their esters to retard polymerization and to serve as clarifying agents. Glycol, glycerol, sorbitol or their esters such as

<sup>138</sup> British P. 148,264, 1919, to Soc. Coralex; *Chem. Abs.*, 1921, 15, 319. See Chapter 42.

<sup>139</sup> S. N. Ushakov and E. M. Obryadina, *Plasticheskie Massy*, 1932, 1, 19; *Chimie et industrie*, 1933, 29, 1418; *Chem. Abs.*, 1933, 27, 4426. *Ind. Eng. Chem.*, 1933, 25, 997.

<sup>140</sup> W. J. R. Evans and R. Hill, British P. 367,001, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 2082.

<sup>141</sup> G. S. Petrov, Russian P. 27,053, 1931; *Chem. Abs.*, 1933, 27, 2260.

<sup>142</sup> French P. 745,316, 1933, to K. Albert G.m.b.H. Chem. Fabr.; *Chem. Abs.*, 1933, 27, 4430.

<sup>143</sup> British P. 369,182, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2320.

<sup>144</sup> E. Beckmann and E. Dehn, *Sitzber. Kgl. preuss. Akad. Wiss., Berlin*, 1918, 1201; *J.S.C.I.*, 1918, 37, 646A. See Chapter 24.

<sup>145</sup> A. Luft, U. S. P. 735,378, Aug. 4, 1903; *J.S.C.I.*, 1903, 22, 1012. See Chapter 13.

<sup>146</sup> H. Lebach, U. S. P. 965,823, July 26, 1910, to Knoll & Co.; *J.S.C.I.*, 1910, 29, 1066.

<sup>147</sup> L. Grognot, U. S. P. 906,219, Dec. 8, 1908; *J.S.C.I.*, 1909, 28, 31. French P. 390,713, 1907, to Produits chimiques de Croissy; *J.S.C.I.*, 1908, 27, 1122. French P. 392,978, 1907; *Chem. Abs.*, 1910, 4, 2745; *J.S.C.I.*, 1909, 28, 17. British P. 16,538, 1908; *J.S.C.I.*, 1909, 28, 152. See Chapter 13.

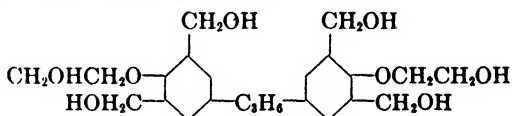
<sup>148</sup> A. Labbé, French P. 468,879, 1913; *J.S.C.I.*, 1914, 33, 975.

<sup>149</sup> U. P. Mehta, U. S. P. 1,458,368, Feb. 12, 1924; *Chem. Abs.*, 1924, 18, 1058.

<sup>150</sup> F. Schmidt, British P. 816,858, 1928, addn. to 804,648, 1923; *Brit. Chem. Abs. B*, 1930, 780; *Chem. Abs.*, 1929, 23, 6337. French P. 664,665, 1928; *Chem. Abs.*, 1930, 24, 981. See other sections of this chapter.

diacetin, glyceryl monopropionate, ether alcohols, acetanilide or mixtures of these substances may also be used. Voss<sup>151</sup> employed polyhydric alcohols such as glycol, glycerol, mannitol or polyvinyl alcohol to modify phenol-formaldehyde resins previously treated with chloroacetic acid. An alkaline solution of sucrose was added to soluble phenol-formaldehyde condensation products by Loetscher<sup>152</sup> in order to produce a varnish resin. Halogenated polyhydric aliphatic alcohols<sup>153</sup> (chlorohydrin,  $\alpha$ ,  $\alpha'$ -dichlorohydrin) have been suggested for treating the condensation product of technical cresol and formaldehyde. Small additions of sodium glycerate were proposed by Heinemann<sup>154</sup> to improve the quality of phenol-aldehyde resins. Berend<sup>155</sup> used glue with the glycerol. Drummond<sup>156</sup> added glycerol acidified with hydrochloric acid to an initial phenol-aldehyde condensate and recommended hypophosphorous acid as a bleaching agent.

Hardenable resins insoluble in water can be made by reacting phenol alcohols with chlorohydrins. Thus, diphenylolpropanetetra-carbinol is dissolved in alcoholic sodium hydroxide and boiled with ethylenechlorohydrin.<sup>157</sup> The viscous product which is obtained has the following structure:



It is convertible into an insoluble infusible resin by heat. When polyhalohydrins are used, the products may contain halogen, and may be further condensed with phenols or organic acids. In this way, soluble resins, useful as ingredients of varnish, are made.<sup>158</sup> A resin may be produced by causing ethylene dichloride or amylene dichlorides to react with a compound containing two or more hydroxyl groups, e.g., resorcinol. The reaction is continued until a tenacious product which does not flow at ordinary temperature is obtained.<sup>159</sup>

To produce phenol-aldehyde resins of ivory-like appearance, Kulas and Pauling<sup>160</sup> heated phenol and formaldehyde in the presence of an acid condensing agent, added an alkaline condensing agent in excess, and then a plasticizer such as amyl alcohol with camphor oil and glycerol. The mixture was boiled to dehydrate it, glacial acetic acid was added, and the resin was hardened by heating at atmospheric pressure. By way of illustration, 0.2 kg. of phenol and 20 g. of water, 0.2 kg. of 30 per cent formaldehyde solution, 5 g. of hydrochloric acid (sp.gr. 1.15) or 5 g. of oxalic acid were boiled together until a resin formed. After this, 0.8 kg. of phenol and 80 g. of water, 2.8 kg. of 30 per cent formaldehyde solution and 0.1 kg. of sodium carbonate were added and the mixture was again boiled until a new formation of resin was completed. After settling, the supernatant liquor was drawn off and the resin thoroughly washed, at first with acidulated water and then with pure water. A mixture of 25 g. of amyl alcohol, 15 g. of camphor oil and 10 g. of glycerol was then added, followed by glacial acetic acid and the resin was hardened by heating at about 110°C. Pechin<sup>161</sup>

<sup>151</sup> A. Voss, U. S. P. 1,892,227, Dec. 27, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 381.

<sup>152</sup> E. C. Loetscher, U. S. P. 1,959,433, May 22, 1934; *Chem. Abs.*, 1934, 28, 4616.

<sup>153</sup> British P. 381,200, 1931, to Chem. Fabr. K. Albert G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 115.

<sup>154</sup> A. Heinemann, U. S. P. 1,441,981, Jan. 9, 1923; *Chem. Abs.*, 1923, 17, 218, 1724. British P. 184,984, 1921; *J.S.C.I.*, 1922, 41, 826A.

<sup>155</sup> L. Berend, U. S. P. 952,724, Mar. 22, 1910; *Chem. Abs.*, 1910, 4, 1530. See other sections of this chapter.

<sup>156</sup> British P. 184,961, 1921, to Lorival Mfg. Co., Ltd.; *Chem. Abs.*, 1923, 17, 188.

<sup>157</sup> E. Fonrobert and F. Lemmer, U. S. P. 1,990,985, Feb. 12, 1935, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1935, 29, 2361. German P. 578,188, 133, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1933, 27, 4430. French P. 719,712, 1931; *Chem. Abs.*, 1932, 26, 3392.

<sup>158</sup> German P. 576,177, 1933, to Firma L. Blumer; *Chem. Abs.*, 1933, 27, 3837. See also Chapter 19.

<sup>159</sup> French P. 772,615, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 1536.

<sup>160</sup> K. Kulas and C. Pauling, U. S. P. 1,582,056, Apr. 27, 1926. U. S. P. 1,414,139, Apr. 25, 1922; *Chem. Abs.*, 1922, 16, 2234. British P. 191,417, 1921; *J.S.C.I.*, 1923, 42, 235A. British P. 159,494, 1920; *J.S.C.I.*, 1922, 41, 475A.

<sup>161</sup> G. Pechin, U. S. P. 1,894,702, Jan. 17, 1933; *Chem. Abs.*, 1933, 27, 2592. British P. 355,634, 1931; *Brit. Chem. Abs. B*, 1931, 985. French P. 690,085, 1929; *Chem. Abs.*, 1930, 24, 6042.

introduced 3 per cent of a mixture containing 90 parts of acetic acid, 7 parts of camphor, 2 parts of glycerol and 1 part of hydrochloric acid into the phenol-formaldehyde product to make the resin more transparent.

Fayolle<sup>150</sup> obtained by the following procedure a product useful in rendering fabrics waterproof and as an electrical insulator. Two parts by weight of sulphuric acid (60°Be.) are added to 1 part of glycerol, the mixture is allowed to cool, and from 1 to 1.5 parts of formalin (40 per cent) are then added. The mixture is again cooled, and, after adding 5 parts of water, 1.25 parts of phenol are slowly poured into it with constant stirring and external cooling. The mixture is then left at rest for 20 hours, when the product will be found as a layer on the surface of the liquid. Gradual hardening occurs on exposure to the air. The formaldehyde may be replaced by methylal and the phenol by cresol. Another formula is: glycerol 1 part, concentrated sulphuric acid 2.2 to 3.3 parts, 40 per cent formaldehyde 1 part, water 0.7-1 part, phenol 2-3 parts. When the amount of phenol is limited to 1 part, the product is obtained by vigorous stirring with 10-20 per cent by weight of concentrated sulphuric acid, but if more phenol is used it may be necessary to heat the mixture on a water bath, and incorporate 10-20 per cent of flowers of sulphur, or to add casein or carbohydrates for otherwise a pitchy substance is formed. When only 0.7 part of phenol is employed, the product is a wax-like solid, soluble in alcohol, and may be utilized in the preparation of varnishes.

#### ETHERS AND ESTERS AS MODIFIERS

Petrov<sup>151</sup> effected the condensation of phenols and formaldehyde in the presence of hydrochloric, phosphoric or benzenesulphonic acids, together with acetic esters of glycerol or cellulose. A mixture of the ingredients, including, however, only part of the aqueous formaldehyde solution, was boiled and after separation of water the remainder of the formaldehyde was introduced. The product was molded and thermally hardened. Bruhat<sup>152</sup> used glyceryl esters such as glyceryl mono-oxalate. For example, the condensation product of phenol with hexamethylenetetramine was mixed with 10 per cent of glyceryl mono-oxalate to yield a material which was partially hardened by storage at 15°C. for several hours before it was molded into shape, and the hardening process completed by heating at 80-100°C. It was molded immediately and hardened subsequently by heating in air. Solutions in alcohol or acetone could be used as a varnish.

Conover<sup>153</sup> heated a fusible resin such as one from phenol and formaldehyde or from glycerol and phthalic acid with diethyl phthalate to produce a homogeneous product which becomes relatively infusible under further heat treatment and is suitable for waterproofing or for the manufacture of molded articles. Butyl palmitate, amyl stearate, esters from aliphatic polybasic acids and polyhydric alcohols,<sup>154</sup> glyceryl monopropionate or monobutyrate<sup>155</sup> all are among the esters that have been proposed. Similarly, polyalkylene glycol aryl ethers or esters such as polyethylene glycol cresyl ether or acetate<sup>156</sup> may be used. For instance, 10 parts of soluble phenol-formaldehyde, made by the use of ammonia as a condensing agent, are heated with 3 parts polyethyleneglycol cresyl ether, prepared by reacting technical cresol with 3 mols of ethylene oxide. The heating is continued for 25 hours at 95-135°C. The product is hard and clear, and can be worked with tools.

<sup>150</sup> E. H. Fayolle, French P. 335,584, 1°03; *J.S.C.I.*, 1904, 23, 195, 448.

<sup>151</sup> G. S. Petrov, British P. 203,124, 1922; *J.S.C.I.*, 1923, 42, 1081A; *Chem. Abs.*, 1924, 18, 595.

<sup>152</sup> J. Bruhat, French P. 575,532, 1923; *Brit. Chem. Abs. B*, 1926, 955. German P. 605,017, 1934; *Chem. Abs.*, 1935, 29, 1904.

<sup>153</sup> C. Conover, U. S. P. 1,592,082, July 13, 1926; *Chem. Abs.*, 1926, 20, 3242.

<sup>154</sup> R. A. Norton, U. S. P. 1,720,051, July 9, 1929, to the Selden Co.; *Chem. Abs.*, 1929, 23, 4308.

<sup>155</sup> H. Mark and H. Schütte, German P. 534,671, 1928; to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1404.

<sup>156</sup> F. Frick, U. S. P. 1,952,243, Mar. 27, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3540. British P. 327,158, 1928; *Chem. Abs.*, 1930, 24, 5118.

Jäger<sup>166</sup> added esters of aromatic hydroxy compounds and inorganic non-volatile acids (the sulphuric or phosphoric acid esters of phenol, naphthol or amyl alcohol) or compounds such as the  $\beta$ -naphthol ester of isopropyl  $\beta$ -naphthalenesulphonic acid to phenol-formaldehyde resins to obtain dull, clouded or opaque white products. The esters can be added when the distillation for the removal of water is almost completed.

Kline<sup>170</sup> allowed about 100 parts of phenol to react with about 200 parts of 40 per cent formaldehyde in the presence of an acid catalyst (oxalic acid) and about 70 parts of diethyl phthalate. After the removal of water, the reaction product is mixed with filling materials (lithopone) in glass, porcelain, enamel-lined or chromium-plated apparatus to obtain substantially colorless resinoids usable in white molding compositions. The surfaces in contact with the resinoid should be free from metals subject to attack by dilute acids. A volatile solvent may be added during the incorporation of filling materials.

Sutherland<sup>171</sup> varied the flexibility of condensation products formed from hydroxyaromatic alcohols and cyclic ethers of polyhydric alcohols by changing the ratio of the quantities used. As a general rule an increase in the amount of the ether increases the flexibility of the final product.

Phenol aldehyde resins may be made somewhat elastic by adding phenyl esters<sup>172</sup> as, for instance, phenyl benzoate or phenyl stearate.<sup>173</sup> Cyclohexanyl esters dissolve stage B resins, and the solutions, when mixed with fillers, are heat-hardenable.<sup>174</sup>

The glycerol ester<sup>175</sup> of lactic acid as a modifier gives clearer products. It is added to the condensation product of phenol and an excess of formaldehyde in the presence of at least 3 per cent of caustic soda. Likewise, the alkyl esters of citric acid have been employed.<sup>176</sup>

Butyl acetate has been used as a medium by means of which iodoform can be incorporated into soluble phenol-formaldehyde resins. In this manner light-sensitive coatings were prepared. In the development process, the resin which has been unacted upon by light remains soluble and can be washed away, and an insoluble product remains where the light was incident upon the film.<sup>177</sup>

The modification of phenolic resins by phenyl derivatives (anisole, acetophenone or methyl benzoate) together with hexamethylenetetramine or hydrobenzamide has been proposed. The constituents should be used in quantities such that the final resin contains approximately equivalent molecular proportions of phenyl and methylene groups. During the reaction ammonia is evolved, and the mixture gradually becomes viscous and solidifies on cooling. At this stage the compound is soluble in alcohol and may be used as a varnish. The reaction may be carried to this stage by boiling a solution of the mixture in alcohol or other non-aqueous solvent. Further heating of the compound produces an infusible, insoluble substance, which may be used as a substitute for amber or as an elec-

<sup>166</sup> A. Jäger, British P. 341,471, 1929, to Herold A.-G.; *Chem. Abs.*, 1931, 25, 5049. French P. 702,823, 1930; *Chem. Abs.*, 1931, 25, 4370.

<sup>170</sup> H. Kline, British P. 353,450, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 1019. French P. 694,047, 1930; *Chem. Abs.*, 1931, 25, 2013. Canadian P. 320,128, 1932; *Chem. Abs.*, 1 32, 26, 3610.

<sup>171</sup> L. T. Sutherland, U. S. P. 1,523,459, Jan. 20, 1925, to Carboloid Products Corp.; *Chem. Abs.*, 1925, 19, 1760. See Chapter 15.

<sup>172</sup> German P. 553,563, 1929, to Herold A.-G.; *Chem. Abs.*, 1932, 26, 5778.

<sup>173</sup> O. A. Cherry, U. S. P. 1,987,787, Dec. 4, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 526.

<sup>174</sup> E. Elbel and O. Stüssenguth, U. S. P. 1,963,579, June 19, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1 34, 28, 5263. E. Elbel and F. Seebach, U. S. P. 1,968,074, July 31, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 6380.

<sup>175</sup> French P. 703,281, 1930, to Herold A.-G.; *Chem. Abs.*, 1931, 25, 4422.

<sup>176</sup> L. Sontag, U. S. P. 1,911,477, May 30, 1933, to General Plastics, Inc.; *Chem. Abs.*, 1933, 27, 4110.

<sup>177</sup> M. C. Beebe, A. Murray and H. V. Herlinger, U. S. P. 1,587,373, June 1, 1926; *Chem. Abs.*, 1926, 20, 2292.

trical insulator. The liquid mixture, after a short heat treatment, may be used as a binder for substances like carborundum.<sup>178</sup>

Esters of inorganic acids, particularly the aryl esters of inorganic oxy-acids, have been used as modifiers of the phenol-formaldehyde resins. Baekeland<sup>179</sup> employed o-cresyl phosphate or a mixture of cresyl phosphates containing a major proportion of the ortho compound. The corresponding silicates, titanates, borates and molybdates also serve as plasticizing agents. As a rule, from 20-60 parts by weight of phenyl ester are added for each 100 parts of the phenol-formaldehyde resin. Ehrenzweig<sup>180</sup> used tricresyl phosphate with hardenable resins having a phenolic base and dissolved the mass in high boiling liquids (triacetin, turpentine oil or glycerol) to make a varnish for coating wires.

Triphenyl phosphate, heated at 320-350°C. with calcium oxide or zinc oxide, resinifies. Small amounts of trioxymethylene are added, corresponding to any phenol that may be liberated. Drying oils may also be incorporated. The product is light amber in color, and is water resistant. It is useful for molding, or in the manufacture of varnish.<sup>181</sup>

#### CELLULOSE ETHERS AND ESTERS

Aylsworth<sup>182</sup> prepared a non-inflammable varnish, for metals, by dissolving a fusible phenol or cresol resin (with or without a hardening agent) and a cellulose ester in a solvent such as acetylene tetrachloride. Softeners (halogenated fatty acids or their esters) and fillers may be added. Bonner<sup>183</sup> dissolved a cellulose ester, e.g., the acetate, in a fluid condensation product of phenol and formaldehyde to form a molding composition.

Cellulose esters were also incorporated with phenol-formaldehyde resin by Jones,<sup>184</sup> who introduced the ester at any stage of the reaction, prior to final hardening. In one procedure, 25 parts of cellulose acetate are dissolved in 212 parts phenol and about 25 parts of a phenol ester added. Then, 212 parts of 40 per cent formalin and about 5 parts concentrated ammonia are introduced and the mixture boiled several hours. The water which separates is decanted and the mass further heated. The product may be used as a coating and fillers may be added.

A mixture of o- and p-hydroxybenzyl alcohol, obtained by condensing formaldehyde or one of its polymers with phenol in the presence of an alkali, with the subsequent addition of an acid such as acetic acid, may be added to compositions having cellulose acetate as a base to regulate the flexibility and durability of films, plates and other articles made from it.<sup>185</sup>

A mixture of viscose, phenol and formaldehyde can be worked or condensed by means of heated rollers, and thus converted into a homogeneous plastic mass, which can be molded or sheeted in a manner similar to rubber. In fact, rubber may be included as one of the ingredients, in which case sulphur may also be added to effect vulcanization under the final action of heat.<sup>186</sup> If, instead of being rolled, these same ingredients are simply heated, solidification takes place and a product resembling shellac in appearance is formed.<sup>187</sup> Fabrics can be waterproofed by coating them first with a rubber composition, then with a layer of cellulose ester

<sup>178</sup> L. V. Redman, U. S. P. 1,209,333, Dec. 19, 1916; British P. 9292, 1914; *J.S.C.I.*, 1915, 34, 623.

<sup>179</sup> L. H. Baekeland, U. S. P. 1,439,056, Dec. 19, 1922; *Chem. Abs.*, 1923, 17, 860.

<sup>180</sup> A. Ehrenzweig, French P. 728,149, 1931; *Chem. Abs.*, 1932, 26, 5777.

<sup>181</sup> A. Runyan, U. S. P. 1,938,642, Dec. 12, 1933, to Sinclair Refining Co.; *Brit. Chem. Abs. B*, 1934, 805.

<sup>182</sup> J. W. Aylsworth, U. S. P. 1,004,830, Apr. 28, 1914; *Chem. Abs.*, 1914, 8, 2268.

<sup>183</sup> W. T. Bonner, U. S. P. 1,173,337, Feb. 29, 1916, 10, 1084.

<sup>184</sup> W. B. Jones, U. S. P. 1,209,165, Dec. 19, 1916; *J.S.C.I.*, 1917, 36, 225.

<sup>185</sup> J. Dupont, U. S. P. 1,317,376, Sept. 30, 1919; *Chem. Abs.*, 1919, 13, 3316.

<sup>186</sup> L. Collardon, U. S. P. 1,128,861, Feb. 16, 1915; *Chem. Abs.*, 1915, 9, 1135.

<sup>187</sup> J. M. Taylor, U. S. P. 1,173,073, Feb. 15, 1916; *Chem. Abs.*, 1916, 10, 1106.



or ether, and finally with a compatible synthetic resin (diphenylolpropane-formaldehyde).<sup>188</sup>

Alkyl ethers of cellulose are suggested as softeners for the synthetic resins. The incorporation of less than 10 per cent ethyl cellulose retards hardening of phenol-formaldehyde compositions.<sup>189</sup> Lilienfeld studied various methods of modifying cellulose ethers, and used a very wide variety of agents, among which were phenolic condensation products.<sup>190</sup> Since the alkyl ethers of cellulose can be made soluble in water, the addition can be made in that solvent.<sup>191</sup> In one method, aqueous solutions of alkyl cellulose ethers were mixed with colloidal dispersions of condensation products made from drying oils and fusible phenol-aldehyde resins. The resins are then converted to the infusible form during or after the manufacture of the film or filaments to give a product which is stable in water.<sup>192</sup> Acetone has also been recommended as a solvent for the homogenizing of cellulose compounds and phenol-formaldehyde resins. In this case, the removal of the solvent leaves a composition which can be powdered, then charged into heated molds to form shaped products.<sup>193</sup> It is also possible to carry out the reaction between phenol, cellulose ester and formaldehyde in the presence of ethyl acetate.<sup>194</sup> The solvent power of phenol for cellulose ethers was utilized by Ushakov<sup>195</sup> to introduce them into the reaction mass, after which formaldehyde and a neutral, acid or alkaline catalyst was added and condensation effected.

Esters of dicarboxylic acids (adipic) have also been used to assist in the preparation of plastic masses from ethyl cellulose and synthetic resins.<sup>196</sup> Weller and Robinson-Bindley<sup>197</sup> effected condensation in the presence of a very small proportion of nitrocellulose or cellulose acetate, the maximum amount of cellulose ester used being about 0.8 per cent of the weight of the phenol. In an example, cresylic acid, formaldehyde, sodium hydroxide and cellulose acetate are mixed, the liquid product is boiled down, baked at atmospheric pressure, and may be further treated in an autoclave. Camphene and nitrocellulose are added to a phenol-formaldehyde condensation product, using acetone as a solvent,<sup>198</sup> to yield a substitute for celluloid. Another way of blending nitrocellulose with a phenol-formaldehyde resin<sup>199</sup> is to treat cellulose with a solution of sulphuric and nitric acid, then, after washing and drying the product, to steep it first in phenol and afterwards in formaldehyde. Finally, 2 per cent of p-dichlorobenzene is added. It is possible to blend phenolic resin with nitrocellulose by reacting phenol with o-benzoyl benzoic acid (in the presence of sulphuric acid), and to mix the reaction product with nitrocellulose and hexamethylenetetramine.<sup>200</sup> The resulting composition is used in lacquers.

A coating composition containing cellulose and synthetic resin can be prepared by mixing cellulose fiber with a varnish formed of a plasticized phenolic resin. After removing the solvent, the residue is rolled until it is homogeneous,

<sup>188</sup> British P. 338,065, 1930, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 2305.

<sup>189</sup> British P. 315,835, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1755.

<sup>190</sup> L. Lilienfeld, U. S. P. 1,217,027 and 1,217,028; *Chem. Abs.*, 1917, 11, 1545.

<sup>191</sup> French P. 35,930, 1928, addn. to 615,876, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 4155.

<sup>192</sup> G. Balle and K. Sponsel, German P. 542,287, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2317. German P. 527,197, 1925; *Chem. Abs.*, 1931, 25, 4705. British P. 308,284, 1927; *Chem. Abs.*, 1920, 24, 239.

<sup>193</sup> German P. 491,396, 1926, to Heinrich Traun & Söhne, vorm. Harburger Gummi-Kamm-Compagnie; *Chem. Abs.*, 1930, 26, 2256.

<sup>194</sup> E. Felger, German P. 541,911, 1928; *Chem. Abs.*, 1932, 26, 2610.

<sup>195</sup> S. N. Ushakov, Russian P. 26,441, 1931; *Chem. Abs.*, 1932, 26, 6080.

<sup>196</sup> W. Hengstmann, French P. 671,728, 1930; *Chem. Abs.*, 1931, 25, 1345.

<sup>197</sup> A. W. Weller and W. T. Robinson-Bindley, U. S. P. 1,368,867, Feb. 15, 1921; *Chem. Abs.*, 1921, 15, 1381. British P. 152,394, 1919; *Chem. Abs.*, 1921, 15, 1060.

<sup>198</sup> W. T. Robinson-Bindley and A. W. Weller, U. S. P. 1,331,127, Feb. 17, 1920; *Chem. Abs.*, 1920, 14, 1196. British P. 134,565, 1918; *Chem. Abs.*, 1920, 14, 808.

<sup>199</sup> British P. 298,798, 1927, to Stabilimenti Chim. Ind.; *Brit. Chem. Abs. B*, 1929, 204.

<sup>200</sup> H. A. Bruson, U. S. P. 1,934,032, Nov. 7, 1933, to Resinous Products & Chemical Co.; *Chem. Abs.*, 1934, 28, 664.

and is thus employed for the preparation of coatings.<sup>201</sup> By treating cresol with allyl alcohol and zinc chloride, Moss and Seymour<sup>202</sup> obtained a resin which was compatible with cellulose acetate.

Compositions containing phenol-formaldehyde and cellulose esters can be made impervious to Röntgen rays or radium emanations by mixing with lead sulphate or lead oxide. For instance, 18 kg. hardenable phenol-formaldehyde resin, 5 kg. wood flour, 5 kg. acetyl cellulose, 70 kg. powdered lead and 2 kg. lead oxide (PbO) are made into a homogeneous mixture.<sup>203</sup> Weber proposed to parchmentize a cellulosic material with sodium zincate, then to treat with phenol and formaldehyde and to condense these substances under heat and pressure.<sup>204</sup>

#### RUBBER-MODIFIED PHENOL-ALDEHYDE RESINS

A hard rubber composition was prepared by Baekeland<sup>205</sup> by mixing with rubber a powdered, brittle phenol-formaldehyde resin representing an intermediate stage of condensation. Catalysts may be present to make the resin infusible on vulcanization of the rubber. Aylsworth,<sup>206</sup> on the other hand, completely hardened a phenol-formaldehyde resin to an infusible and insoluble condition before incorporation with rubber, and exposed the resin in powdered form to a temperature of about 260°C. to remove any free phenol, moisture or ammonia. The hardened condensation product was used in proportions varying between 30 and 90 per cent of the total composition. Vulcanization was carried out at the usual vulcanizing temperature.

Another procedure, recommended by Aylsworth,<sup>207</sup> was the treatment of a hard, porous sponge of a completely condensed product of phenol and formaldehyde by boiling for several hours with a 10 per cent solution of caustic soda or potash. After washing, 2-4 parts of the residue were mixed with 1-3 parts of rubber, sulphur was added and the composition vulcanized by heating. The molded and vulcanized material when used for battery jars containing a strongly alkaline electrolyte was treated with caustic alkali to remove any excess of the vulcanizing agent. Benjamin<sup>208</sup> mixed rubber stock and a vulcanizing agent with asbestos, mica or other mineral filler, the particles of which are coated with a primary soluble resinous condensation product of phenol and formaldehyde, and hardened the mixture by heating. A resilient gasket or packing material can be made from this composition. The completed material contains less than 1 per cent of uncombined sulphur. For the preparation of another rubber composition,<sup>209</sup> commercial phenol is mixed with an equal volume of 40 per cent formalin and 5 per cent ammonia solution, and the mixture is maintained at about 80°C. until a plastic mass results. Twenty per cent of this mass is mixed with 40 per cent rubber, 7-8 per cent sulphur and the usual fillers. The composition is vulcanized for 2 hours at 138°C. A phenolic rubber composition capable of being coated onto cloth or paper and then vulcanized was prepared by Satow.<sup>210</sup> The composition contained phenolic resin, rubber, wood flour, asbestos, sulphur, magnesium carbonate and solvent.

A mixture of rubber, vegetable ivory and phenol-formaldehyde resin in equal proportions was used by Wiechmann<sup>211</sup> as a plastic composition. Rubber or rub-

<sup>201</sup> F. Groff, U. S. P. 1,865,628, July 5, 1932, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 4487.

<sup>202</sup> W. H. Moss and G. W. Seymour, U. S. P. 1,940,727, Dec. 26, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1934, 28, 1560. W. H. Moss and G. W. Seymour, Canadian P. 324,633, 1932, to C. Drevius; *Chem. Abs.*, 1932, 26, 4970.

<sup>203</sup> M. Weger, U. S. P. 1,918,996, July 18, 1933, to Bakelite G.m.b.H.; *Chem. Abs.*, 1933, 27, 4943.

<sup>204</sup> H. C. P. Weber, U. S. P. 1,871,641, Aug. 16, 1932; *Chem. Abs.*, 1932, 26, 6081.

<sup>205</sup> L. H. Baekeland, U. S. P. 1,200,892, Oct. 10, 1916; *Chem. Abs.*, 1916, 10, 3179.

<sup>206</sup> J. W. Aylsworth, U. S. P. 1,111,234, Sept. 22, 1914; *Chem. Abs.*, 1914, 8, 3634.

<sup>207</sup> J. W. Aylsworth, U. S. P. 1,092,511, Apr. 7, 1914; *Chem. Abs.*, 1914, 8, 1878.

<sup>208</sup> E. O. Benjamin, U. S. P. 1,409,275, 1,409,276 and 1,409,277, March 14, 1922; *Chem. Abs.*, 1922, 16, 1841.

<sup>209</sup> A. Speedy and A. P. Crouch, British P. 171,803, 1920; *J.S.C.I.*, 1922, 41, 67A.

<sup>210</sup> T. Satow, U. S. P. 1,748,788, Feb. 4, 1930; *Chem. Abs.*, 1930, 24, 1766.

<sup>211</sup> F. G. Wiechmann, U. S. P. 1,067,355, July 22, 1913; *Chem. Abs.*, 1913, 7, 3087.

ber substitute, vegetable albumin and phenol-formaldehyde resin may be incorporated on mixing rolls.<sup>212</sup>

Plauson<sup>213</sup> incorporated rubber with condensation products of formaldehyde and phenol, acetone or furfural by homogenizing the substances in the presence of a liquid which exerts a solvent or a swelling action upon both ingredients (chlorohydrin or cyclohexanol).<sup>214</sup> Fillers, solvents or sulphur may be added and the product vulcanized. To obtain a varnish 20 parts of phenol-aldehyde resin, 5 parts of rubber and 50 parts of cyclohexanol may be used. For a molding mixture, 10 parts of rubber, 90 parts of resin, 30 parts of  $\beta$ -dichlorohydrin and 20 parts of cyclohexanol, with or without fillers and sulphur, may be used, the solvents being expelled by evaporation.

Raw rubber can be mixed with fusible phenol resins on cold rolls or in cooled mixing machines. On heating to 180°C. in molds the material becomes insoluble and has the appearance and characteristic properties of an elastic, light-colored vulcanite. The rubber in such compositions can be vulcanized either by incorporating a small percentage of sulphur in the original mixture or by subsequent surface-vulcanization with sulphur chloride.<sup>215</sup> Hydrocarbon polymers other than natural rubber have been used for incorporation in phenol-formaldehyde resins. Thus the polymers of unsaturated hydrocarbons obtained from cracked petroleum have been employed.<sup>216</sup>

Hopkinson<sup>217</sup> incorporated rubber with vulcanizing, compounding and filling materials by suspending, emulsifying or dissolving the materials in water, adding them in this form to latex, and drying the mixture. Insoluble solids (gums, phenol-aldehyde and other resins, stearic acid, paraffins and waxes) are dissolved in organic solvents and the solutions are emulsified with water. The aqueous mixture may be dried by spraying in a heated atmosphere or in the usual drying chambers and can then be used for molding. Also, latex can be treated with phenol, and formaldehyde added afterwards.<sup>218</sup> If sufficient formaldehyde is added, coagulation takes place.<sup>219</sup> In another proposal a plastic material is obtained from a phenol and an aldehyde which is included in an aqueous dispersion of latex. The mixture is heated in an autoclave to give a product which may be vulcanized.<sup>220</sup> Bradley and Cadwell<sup>221</sup> heated a mixture of rubber, a vulcanizing agent and a condensation product of formaldehyde with an aliphatic amine, and obtained vulcanized products.

McGavack,<sup>222</sup> to produce rubber compositions which can be molded, dissolved 15 kg. of crepe rubber in 400 kg. of carbon tetrachloride and passed chlorine into the solution till the rubber had absorbed twice its own weight. He then added 30 kg. of phenol dissolved in an equal weight of 40 per cent formaldehyde solution and mixed the solutions thoroughly. The mixture was heated for 2 hours under reflux, added to boiling water and the excess of solvent, chlorine, hydrochloric acid, formaldehyde and phenol removed by washing several times. The product was milled, pulverized, dried at 95°C. and then molded at 175°C. under a pressure of about 3000-4000 pounds per square inch. It had a density of about 1.4.

<sup>212</sup> F. G. Wiechmann, U. S. P. 1,067,356, July 22, 1913; *Chem. Abs.*, 1913, 7, 3037.

<sup>213</sup> H. Plauson, British P. 193,524, 1921, to Plauson's (Parent Co.) Ltd.; *Chem. Abs.*, 1923, 17, 3429.

<sup>214</sup> British P. 176,008, 1920, to Traun's Forsch. lab. G.m.b.H.; *J.S.C.I.*, 1922, 41, 357A.

<sup>215</sup> British P. 214,124, 1923, to Felten & Guillaume Carlewark A.-G.; *J.S.C.I.*, 1924, 43, 527B.

<sup>216</sup> F. A. Agar and A. Runyan, U. S. P. 1,945,719, Feb. 6, 1934, to Sinclair Refining Co.; *Chem. Abs.*, 1934, 1022.

<sup>217</sup> E. Hopkinson, British P. 204,487, 1923; *Chem. Abs.*, 1924, 18, 1068.

<sup>218</sup> C. Hayes, E. N. Madge and F. C. Jennings, U. S. P. 1,890,578, Dec. 13, 1932, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 1783.

<sup>219</sup> French P. 630,983, and addn. 33,927, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 3827.

<sup>220</sup> French P. 771,747, 1934, to Società italiana Pirelli; *Chem. Abs.*, 1935, 29, 1535. British P. 424,312, 1934; *Brit. Chem. Abs.*, 1935, 368.

<sup>221</sup> C. E. Bradley and S. M. Cadwell, U. S. P. 1,444,865, Feb. 13, 1923, to Naugatuck Chemical Co.; *Chem. Abs.*, 1923, 17, 1352.

<sup>222</sup> J. McGavack, U. S. P. 1,555,181, Sept. 29, 1925, to Revere Rubber Co.; *Chem. Abs.*, 1925, 19, 3616. British P. 223,873, 1923; *J.S.C.I.*, 1925, 44, 463B. See also Chapter 55.

A reaction product resembling hard rubber is formed from rubber and an aldehyde with sulphuric acid as condensing agent.<sup>223</sup> The condensation may also be carried out between rubber, an aldehyde and phenol. Thus vulcanized rubber can be treated, according to McGavack,<sup>224</sup> with a rubber solvent such as benzene and then with chlorine, phenol and formaldehyde in a manner similar to that described to obtain a product resembling hard rubber.<sup>225</sup>

Uncured rubber and a phenol-aldehyde resin can be united by molding under heat and pressure, forming a hard material, according to Warwick and Warwick.<sup>226</sup> Material usable for electrical insulation was obtained by Kulas<sup>227</sup> by adding 100 parts of pulverized scrap or waste rubber or 50 parts of rubber and 50 parts of filler or coloring material to the viscous solution of a phenol-aldehyde condensation product dissolved in 50 parts of acetone or alcohol. The mixture was stirred and gently boiled, the solvent recovered and the residual material rapidly calendered to expel volatile constituents. It was seasoned at 30-40°C. for about 14 days, molded and dried at a temperature gradually increased to 160°C. Finely divided ebonite<sup>228</sup> may be incorporated with a phenol-formaldehyde resin by swelling the ebonite with the molten resin and molding when the gel state is reached.

Naunton and Siddle<sup>229</sup> investigated the possible utility of phenol-formaldehyde and of polybasic acid-polyhydric alcohol (alkyd) resins in soft and hard vulcanized rubber. Phenol-formaldehyde resins are very difficult to disperse during mastication and it was found better to dissolve the resin in concentrated sodium hydroxide, add this to latex, coagulate with carbon dioxide, wash, dry and masticate the finely divided precipitate. Some alkyd resins have a retarding effect on vulcanization and one such resin was found which had pronounced "anti-scorching" power. In hard rubber, phenol-aldehyde resins protect the surface from light, increase the resistance to heat, to hydrocarbon solvents and to mineral oils.

A method for attaching rubber to a rigid material, such as metal, is to interpose a layer of a composition containing phenol-formaldehyde resin and vulcanizable rubber. The application of heat and pressure hardens the phenol-formaldehyde composition and consequently the rubber becomes bound to the metal. The cement is composed of rubber, carbon black, sulphur, methylene p-toluidine and a phenol-formaldehyde condensation product.<sup>230</sup> A cement for uniting resin-impregnated fabric to metal contains a solution of phenol-aldehyde resin and rubber.<sup>231</sup>

#### LIMED COMPOSITIONS

A large number of resinous products contain oxides or carbonates of calcium or magnesium in admixture with phenol-formaldehyde resins. A typical example of such a limed composition is made by treating fusible phenol-formaldehyde resin with calcium hydroxide to convert the phenol groups to phenolates. The cooled or solidified product is mixed with a compound containing active methylene

<sup>223</sup> J. McGavack, U. S. P. 1,640,363, Aug. 30, 1927, to Revere Rubber Co.; *Chem. Abs.*, 1927, 21, 3490.

<sup>224</sup> J. McGavack, U. S. P. 1,640,364, Aug. 30, 1927, to Revere Rubber Co.; *Chem. Abs.*, 1927, 21, 3490.

<sup>225</sup> H. Frood, British P. 176,405, 1920; *J.S.C.I.*, 1922, 41, 335A.

<sup>226</sup> B. O. Warwick and M. Warwick, British P. 336,292, 1929, to Warwick's Time Stamp Co.; *Chem. Abs.*, 1931, 25, 1957.

<sup>227</sup> K. Kulas, U. S. P. 1,688,500, Oct. 23, 1928; *Brit. Chem. Abs. B*, 1929, 531. Canadian P. 268,515, 1927; *Chem. Abs.*, 1927, 21, 2363.

<sup>228</sup> French P. 728,660, 1931, to Comp. general d'electricite; *Chem. Abs.*, 1932, 26, 5711.

<sup>229</sup> W. J. S. Naunton and F. J. Siddle, *India Rubber J.*, 1931, 82, 535, 561; *Chem. Abs.*, 1932, 26, 1151.

<sup>230</sup> O. A. Thompson, U. S. P. 1,931,309, Oct. 17, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1934, 28, 374. British P. 388,776, 1933; *Chem. Abs.*, 1933, 27, 5909.

<sup>231</sup> G. E. Landt, British P. 419,901, 1934, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1935, 29, 2627.

groups to transform the fusible resin into one which is infusible and insoluble. Filling materials are added, and the product is molded.<sup>232</sup>

Phenol and formaldehyde may be condensed in the presence of mixtures of magnesium carbonate and magnesium oxide. The resinous product is kneaded and molded to form masses resembling yellow ivory,<sup>233</sup> suitable in density for use in the manufacture of billiard balls. When nigrosine and wood flour are also added, and the mixture dried at 75°C. under reduced pressure, a product is formed which can be molded cold under high pressure and hardened at 160°C.<sup>234</sup> To assist in taking up the 4-5 per cent water in the separated resin, plaster of Paris may be added.<sup>235</sup> The procedure is to take 100 parts of crude coal-tar acids, and mix with 120 parts of ground magnesium-formaldehyde mixture (made by grinding in a pebble mill 30 parts of calcined magnesium oxide and 150 parts of aqueous 40 per cent formaldehyde solution). Two hundred parts of saturated brine is added, and the mixture is allowed to stand in the cold with slow agitation until all the formaldehyde is consumed. When the reaction is over, the water is decanted, and the resinous mass is dehydrated by mixing with 54 parts of powdered plaster of Paris. One hundred parts of wood flour containing 2 parts of aluminum palmitate and 2 parts of carbon black are now incorporated by means of a pebble mill.

The temperature and time of heating may be varied<sup>236</sup> in order to alter the properties of the product. In many experiments the temperature during the initial condensation was 90-95°C., and the time of reaction about 30 minutes. A number of substances other than those mentioned above have also been used. Among these are iron oxides, zinc oxide, salts of fatty or resin acids,<sup>237</sup> sodium carbonate and a mixture of sodium carbonate with sodium borate.<sup>238</sup>

In another process,<sup>239</sup> the fusible phenol-formaldehyde resin is heated at 175°C. with a solid basic oxide (CaO, MgO, NaOH) to neutralize the hydroxyl groups of any free phenol or of the resin itself. The product needs no mechanical plasticizing, but can be pulverized, mixed with fillers and a methylene-containing agent, and hot-molded. Portland cement has been mixed with a phenol-aldehyde resin, asbestos and solvents (e.g., acetone, methyl ethyl ketone) to give an adhesive suggested for use with linoleum.<sup>240</sup>

Hexamethylenetetramine is used to assist setting of limed resins in the molding operation, without causing excessively rapid hardening.<sup>241</sup> A method described by Redman<sup>242</sup> calls for boiling in a still for 2 hours at about 200°C., with continuous rapid stirring, 74 pounds calcium hydroxide, 877 pounds phenol-formaldehyde condensation product (from 1.25 mols phenol and 1 mol formaldehyde). The mass is cooled, ground and mixed with 52.5 pounds of hexamethylenetetramine. Then the product is pulverized, mixed with fillers and molded in a hot press. In the initial step (the treatment of the phenol-formaldehyde with lime), it is desirable to calculate the lime addition as substantially equivalent to the hydroxyl of the resin, but a somewhat smaller proportion of lime may be used with good results.<sup>243</sup>

When sulphuric acid is used as the catalyst in the preparation of a phenolic

<sup>232</sup> French P. 697,525, 1930, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 3186.

<sup>233</sup> German P. 359,825 and 359,826, 1922, to H. Rommler A.-G.; *J.S.C.I.*, 1923, 42, 281.

<sup>234</sup> H. M. Weber, U. S. P. 1,536,253, June 5, 1925, to Ellis-Foster Co.; *J.S.C.I.*, 1925, 44, 601B. Carleton Ellis, U. S. P. 1,580,425, April 13, 1926, to Ellis-Foster Co.; *Brit. Chem. Abs. B*, 1926, 596.

<sup>235</sup> Carleton Ellis, U. S. P. 1,691,271, Nov. 13, 1928; *Brit. Chem. Abs. B*, 1929, 566.

<sup>236</sup> H. M. Weber, U. S. P. 1,692,524, Nov. 20, 1928, to Ellis-Foster Co.; *Brit. Chem. Abs. B*, 1929, 256.

<sup>237</sup> British P. 305,237, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1929, 23, 4837. French P. 667,915, 1929; *Chem. Abs.*, 1930, 24, 1530. French P. 717,635, 1931; *Chem. Abs.*, 1932, 26, 2880.

<sup>238</sup> G. Bia, French P. 638,887, 1926, to J. E. Douzal de Granville de Brelize; *Chem. Abs.*, 1929, 23, 489.

<sup>239</sup> British P. 357,259, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 1107.

<sup>240</sup> R. D. Bonney and A. G. De Boer, U. S. P. 1,991,007, Feb. 12, 1935, to Congoleum-Nairn, Inc.; *Chem. Abs.*, 1935, 29, 2262.

<sup>241</sup> Carleton Ellis, U. S. P. 1,579,195, Mar. 30, 1926; *Chem. Abs.*, 1926, 20, 1696. See also French P. 696,390, 1930, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 2867.

<sup>242</sup> L. V. Redman, A. J. Weith and F. B. Brock, U. S. P. 1,811,808, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 4983.

<sup>243</sup> L. V. Redman, A. J. Weith, F. P. Brock, U. S. P. 1,924,514, Aug. 29, 1933, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 5492.

resin, its disintegrating effect is prevented, Harrison<sup>244</sup> states, by using aluminum or magnesium compounds instead of barium hydroxide and either a barium soap or a soap-forming acid. The basic oxides,<sup>245</sup> hydroxides or carbonates of magnesium, iron, zinc, sodium or potassium in sufficient amount to neutralize all free phenol, are suggested as additions for obtaining good molding properties.

The modifying action of soaps was utilized by Rosenblum.<sup>246</sup> Phenol and formaldehyde are condensed in the presence of zinc oleate or rosinate to the extent of 7.5 per cent (calculated as oxide) of the phenol. Condensation is continued until a resin is obtained which is soluble in varnish solvents. Organic salts of calcium, barium, strontium, sodium, lead, manganese or cobalt may be substituted.

Ellis<sup>247</sup> found that an alkaline-earth base so alters the resin that it becomes particularly adaptable for hot molding. For example, 1 mol of phenol, 0.25 the combining proportion of barium hydroxide and aqueous formaldehyde in an amount equal to the weight of phenol are heated and stirred together at 80-90°C. for 2-3 hours, when the solution is ready to be mixed with a filler.

A synthetic resin, made by condensing a phenol with formaldehyde in the presence of lime, and then in the presence of sulphuric acid, can be mixed with a small amount of montan wax and alkaline catalyst. Hexamethylenetetramine, and fillers, are then added in order to convert the product into a moldable resin.<sup>248</sup>

A molding powder which resembles the limed resins is made up in the following manner: in an open vessel heat a mixture of rosin (4 parts), calcium oxide (1 part) and formalin (4 parts); pulverize the product, and to 450 parts of the powdered mixture add wood flour (300 parts), Portland cement (4 parts) and heavy mineral oil (10 parts) which has been baked to a paste with calcium carbonate (5 parts); harden with about 8 per cent hexamethylenetetramine. Synthetic phenolic resins may be incorporated with the rosin.<sup>249</sup> Resinous compositions resistant to penetration by x-rays or radium rays may be prepared by causing phenolic compounds of lead, uranium, thorium or thallium to react with an aldehyde.<sup>250</sup>

Other products which are similar to the limed phenol-formaldehyde resins are the limed phenol-carbohydrate resins described by Meigs.<sup>251</sup> The phenol-carbohydrate resins are made by condensing phenol with sugar (e.g., dextrose). These resins are subjected to a treatment resembling that by which the limed phenol-formaldehyde products are formed; namely, neutralization with calcium hydroxide, reaction with hexamethylenetetramine, grinding, addition of wood flour and molding at 150-180°C.

#### MISCELLANEOUS MODIFIERS

Various organic acids have been added to phenolic resins, usually in the A (initial) stage of condensation. The purpose which the acid is intended to serve varies widely from case to case, but usually the reaction involved is one of condensation in which hydroxyl groups of the resin take part.

Lactic acid of 50-60 per cent concentration may be incorporated with the initial liquid condensation product of phenol and formaldehyde (in the proportion of 80 parts of the condensation product to 45 parts of the acid) to yield a molding composition. The mixture is heated at 100-110°C. until condensation has proceeded so far that the product no longer adheres firmly to a clean metallic surface. At room tem-

<sup>244</sup> R. T. Harrison, British P. 387,075, 1931, to Chloride Elec. Storage Co., Ltd.; *Brit. Chem. Abs.* B, 1933, 277.

<sup>245</sup> E. Elbel, German P. 556,927, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1933, 27, 434. German P. 598,811, 1934; *Chem. Abs.*, 1934, 28, 7443. British P. 357,259, 1930, to Bakelite Corp; *Chem. Abs.*, 1932, 26, 6166.

<sup>246</sup> I. Rosenblum, U. S. P. 1,808,716, June 2, 1930; *Chem. Abs.*, 1931, 25, 4422.

<sup>247</sup> Carleton Ellis, U. S. P. 1,903,809, Apr. 18, 1933, to Ellis-Foster Company; *Chem. Abs.*, 1933, 27, 3351.

<sup>248</sup> E. F. Fiedler, British P. 387,932, 1933, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 4702.

<sup>249</sup> W. H. Boorne, British P. 345,472, 1930; *Brit. Chem. Abs.* B, 1931, 687.

<sup>250</sup> M. Weger, U. S. P. 1,918,996, July 18, 1933, to Bakelite G.m.b.H.; *Chem. Abs.*, 1933, 27, 4943.

<sup>251</sup> J. V. Meigs, U. S. P. 1,593,342, July 20, 1926; *Chem. Abs.*, 1926, 20, 3242. U. S. P. 1,877,417, Sept. 13, 1932, to Plastix Corp.; *Chem. Abs.*, 1933, 27, 200.

perature this product forms a very viscous syrup, and filling material (asbestos, wood flour or china clay) may be readily added to make a molding composition which can be hardened by baking.<sup>252</sup> Clear, transparent products<sup>253</sup> are made by condensing 1 mol of phenol and 15 mols of formaldehyde in a solution which is sufficiently alkaline for the resin to remain in solution during the condensation, and only such acids or bases as form salts which do not cause turbidity are used as hardening agents. Lactic acid and potash are suggested as being useful for this purpose.

Jäger<sup>254</sup> employed salicylic acid as a modifier (see also Chapter 17). For example, he condensed 1 part of phenol with 22-3 parts of 30 per cent formaldehyde in the presence of 0.35 part of an alkaline salt of a fatty acid (sodium stearate), heated the mass 19 minutes at 70°C., dehydrated *in vacuo* and added 1.8 mols of salicylic acid per 1 mol of alkali. The resin is useful for the manufacture of artificial horn. Castor oil or glycerol may be added.

Pyromucic acid is heated under pressure at 120-150°C., together with phenols and sulphuric, hydrochloric or phosphoric acid. Formaldehyde, or its polymers, and filling materials may also be introduced into the reaction mixture. The products, which are partly soluble in alcohol and acetone and completely soluble in benzene, are used for making a substitute for vulcanite and for the preparation of varnishes.<sup>255</sup> Aylsworth<sup>256</sup> employed a number of organic acid anhydrides, including benzoic, phthalic, acetic and stearic. These absorb ammonia by forming amides, and increase the toughness of the product. Stage A resins have been made from a mixture of phenol, formaldehyde, fatty acids and ammonia. The ammonia combines with the aldehyde. As soon as the soluble resin is formed, the reaction is checked by neutralization of the excess free acid.<sup>257</sup>

By the use of polycarboxylic acids, notably phthalic, naphthalic, diphenic, maleic, fumaric, malic, succinic and tartaric acids, Norton<sup>258</sup> was able to prepare non-turbid resins for the production of so-called non-breakable glass substitutes, transparent fountain pen barrels, and imitations of jewelry stones. For example, 1000 parts of phenol are caused to react with 1000 parts of formaldehyde in the form of a 40 per cent solution, in the presence of 2 parts of sodium carbonate. Fifty to 100 parts of sodium acid phthalate are then incorporated, and the water formed by the reaction is allowed to volatilize. The product is free from turbidity.

When o-phthalaldehydic acid condenses with phenols or phenol ethers, gummy products are formed<sup>259</sup> from which crystalline phthalides can be obtained. The phthalides<sup>260</sup> may be used as plasticizers and softeners not only of phenolic resins, but of the alkyl and urea resins also (see Chapters 11, 31, 47, 53).

Petrov<sup>261</sup> condensed phenol with formaldehyde in the presence of acidic or basic catalysts, and after cooling to 40-50°C. mixed naphthenic acids obtained by the oxidation of petroleum products and then dissolved the resulting semi-fluid substances in alcohol. He proposed their use for insulating varnishes or as a binding material for molding compositions. (See Chapter 16.)

Schmidt<sup>262</sup> employed small quantities of phosphoric or oxalic acid in order to vary the  $p_H$  of phenol-formaldehyde resins. The neutralized plastic resin is brought to a  $p_H$  of approximately 4 or 5 by kneading it with either of these acids.

<sup>252</sup> W. Petersen and E. V. Clark, British P. 179,586, 1921; *J.S.C.I.*, 1922, 41, 509A.

<sup>253</sup> British P. 357,276, 1930, to Kunstharzfabrik F. Pollak Ges.; *Chem. Abs.*, 1932, 26, 6166

<sup>254</sup> A. Jäger, British P. 281,537, 1927, to Herold A.-G. French P. 666,184, 1929; *Brit. Chem. Abs. B.*, 1928, 101.

<sup>255</sup> German P. 342,365, 1920, to H. Plauson's Forschungsinstitut G.m.b.H.; *J.S.C.I.*, 1922, 41, 111A.

<sup>256</sup> J. W. Aylsworth, U. S. P. 1,020,594, Mar. 19, 1912; *Chem. Abs.*, 1912, 6, 1377. U. S. P. 1,046,420, Dec. 3, 1912; *Chem. Abs.*, 1913, 7, 712. U. S. P. 1,102,634, July 7, 1914; *Chem. Abs.*, 1914, 8, 3127.

<sup>257</sup> G. S. Petrov, Russian P. 20,835, 1933; *Chem. Abs.*, 1934, 28, 5941.

<sup>258</sup> R. A. Norton, U. S. P. 1,720,052, July 9, 1929, to Selden Co.; *Chem. Abs.*, 1929, 23, 4308.

<sup>259</sup> M. M. Brubacker and R. Adams, *J.A.C.S.*, 1927, 49, 2283.

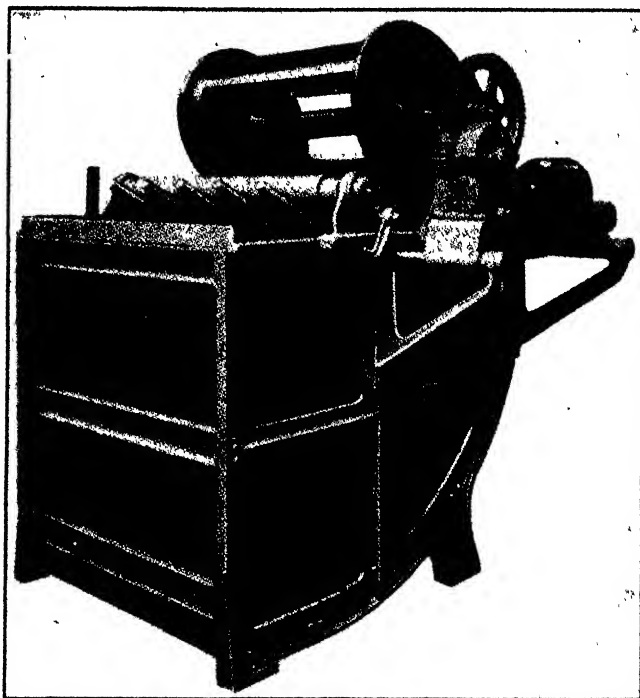
<sup>260</sup> A. O. Jaeger, U. S. P. 1,941,474, Jan. 2, 1934, to Selden Co.; *Chem. Abs.*, 1934, 28, 1880.

<sup>261</sup> G. Petrov, German P. 437,612, 1924; *Brit. Chem. Abs. B.*, 1927, 452. G. S. Petrov and S. I. Dimakov, Russian P. 31,530, 1933; *Chem. Abs.*, 1934, 28, 3256.

<sup>262</sup> F. Schmidt, U. S. P. 1,978,821, Oct. 30, 1934; *Chem. Abs.*, 1935, 29, 252.

If a  $p_H$  below 2.5 is maintained during the hardening operation, the product is unstable, and if the  $p_H$  is above 5.5, the hardening under pressure and heat proceeds too rapidly. (See Chapter 16).

Cacodylic acid,  $(CH_3)_3AsOOH$ , has been incorporated with phenolic resins. The object in this case is to produce a resinous coating containing arsenic. Such a coating may be applied when the destructive action of parasites is to be prevented, for instance, on surfaces which are to be exposed to the action of marine growths.<sup>203</sup>



Courtesy H. W. Butterworth & Sons Co.

FIG. 72.—Dyeing Machine Made of Haveg.

In preparing insulating compositions for incasing electric coils, Baekeland<sup>204</sup> used solvents boiling above 120°C. such as naphthalene, xylene, nitrobenzene and other hydrocarbons or their homologues or mixtures of these, to reduce the shrinkage of the resin and soften it at high temperatures. He also employed permanently fusible resins, e.g., those from phenol and formaldehyde. Aylsworth<sup>205</sup> used similar substances, and also dinitrobenzene, acetanilide and ricinoleic acid, incorporating these softeners with the resin by mixing at 175°C. Small quantities of softening agents eliminate the brittleness and inflexibility which is an inherent property of hardened phenol-formaldehyde resins. Baekeland also made particles or fragments of an infusible composition containing a phenolic condensation product in solid solution with naphthalene, anthracene or other solvent of high

<sup>203</sup> A. Heinemann, U. S. P. 1,176,056, Mar. 21, 1916; *Chem. Abs.*, 1914, 8, 1441.

<sup>204</sup> L. H. Baekeland, U. S. P. 1,156,452, Oct. 12, 1915; *Chem. Abs.*, 1915, 9, 3334.

<sup>205</sup> J. W. Aylsworth, U. S. P. 1,111,285, Sept. 22, 1914; *J.S.C.I.*, 1914, 33, 1063.



boiling point, and after transformation into the final state, welded them together into coherent masses under the action of heat and pressure.<sup>266</sup>

Phenol-formaldehyde resins prepared in the presence of 2 per cent camphor, which is subsequently removed by steam distillation, are said to be odorless and non-sticky, pale yellow to dark brown, soluble in caustic alkalis, alcohols, acetone, formic and acetic acids, insoluble in cold benzene and carbonates.<sup>267</sup>

Cyclohexane, cyclohexanol or its esters, and cyclohexanone were used as plasticizers by Elbel and Seebach.<sup>268</sup> The nature of the product is determined not only by the plasticizer but also by the amount of hexamethylenetetramine, which is used as an initial ingredient of the resin.

Sulphur compounds were early used in connection with phenolic resins. McCoy<sup>269</sup> prepared a factice from oil with 5 per cent sulphur monochloride. One hundred and twenty parts of this factice, dissolved in 300 parts of phenol, are added to 320 parts formalin, and the temperature is raised to 100-125°C. until the water is driven off. On further heating, there is formed an insoluble, infusible mass which is resistant to water. Tubes of paper pulp can be impregnated with sulphur-phenol-formaldehyde resin to render them waterproof.<sup>270</sup> Treatment of phenol-formaldehyde resins with sulphur monochloride gives products which are useful for making electrical and thermal insulators.<sup>271</sup>

Modification of phenol-formaldehyde resins can also be accomplished by adding other synthetic resins. Many of these are considered in the chapters of this book (see Chapters 30, 46, 51, 58), where the particular resin is discussed.

Kollek and Engels<sup>272</sup> observed that the polymerization products of alkylene oxides (particularly ethylene oxide) increase the elasticity of phenol-formaldehyde resins. Another suggestion calls for the addition of phenolic resins to resins prepared from sunflower husks. The resultant product may be used in varnishes.<sup>273</sup>

Crystalline hexamethylenetetramine-triphenol, prepared by boiling an alcoholic solution of hexamethylenetetramine and phenol, is a plasticizing agent, and can be used to convert overcured resins into products which can be hot-molded.<sup>274</sup> Resins which are not sufficiently hardened can be made solid by the addition of hexamethylenetetramine.<sup>275</sup> According to McCoy, the catechol tannins are of value in regulating the hardening of resins, especially when it is undesirable to introduce material which has a deleterious effect on the dielectric strength of the resin. The hardening action of the catechols is a result of reaction with formaldehyde, and a catalytic influence.<sup>276</sup>

Phenolic resins can be brought into the form of a water suspension by running them directly from the reaction zone into water, and dispersing with the assistance of gum arabic.<sup>277</sup> When a colloidal solution of a resin is added to a colloidal solution of another resin, or of casein, a fatty acid or a cellulose ester, mutual precipitation of the colloids is likely to occur. The precipitate may be dried, powdered and hot-molded.<sup>278</sup>

<sup>266</sup> L. H. Baekeland, U. S. P. 1,259,472 and 1,259,473, Mar. 19, 1918; *Chem. Abs.*, 1918, 12, 1502.

<sup>267</sup> German P. 396,510, 1910, to J. Perl & Co. Komm.-Ges. Chem. Fabr.; *Brit. Chem. Abs. B*, 1934, 879.

<sup>268</sup> E. Elbel and F. Seebach, U. S. P. 1,968,074, July 31, 1934, to Bakelite G. m. b. H.; *Chem. Abs.*, 1934, 28, 6330.

<sup>269</sup> J. P. A. McCoy, *British P.* 13,657, 1913; *J.S.C.I.*, 1914, 33, 653. See also Chapter 60.

<sup>270</sup> F. A. Burningham, G. A. Richter, W. B. Van Arsdell and D. H. White, U. S. P. 1,396,201, Nov. 8, 1921; *Chem. Abs.*, 1922, 16, 657.

<sup>271</sup> A. A. Samuel, U. S. P. 1,704,629, Mar. 5, 1929; *Chem. Abs.*, 1929, 23, 1971.

<sup>272</sup> L. Kollek and W. Engels, German P. 560,703, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1114. See also French P. 774,176, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2261.

<sup>273</sup> G. S. Petrov and S. I. Dimakov, Russian P. 31,530, 1933, addn. to 20,747, 1931; *Chem. Abs.*, 1934, 28, 3256.

<sup>274</sup> H. M. Weber, U. S. P. 1,720,406, July 9, 1929, to Ellis-Foster Co.; *Brit. Chem. Abs. B*, 1929, 948.

<sup>275</sup> A. A. Samuel, French P. 700,789, 1929; *Chem. Abs.*, 1931, 25, 3856.

<sup>276</sup> J. P. A. McCoy, U. S. P. 1,269,627, June 18, 1918; *Chem. Abs.*, 1918, 12, 1916.

<sup>277</sup> H. C. Cheestham, U. S. P. 1,976,433, Oct. 9, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 7563.

<sup>278</sup> A. Spitzer, Austrian P. 137,563, 1934; *Chem. Abs.*, 1934, 28, 5694.

The use of dyestuffs for coloring purposes is, of course, common in the resin industry, but their use for the purpose of modification is infrequent. By incorporating a diazo compound with a synthetic resin before completing the condensation, colored resins and oil-soluble dyestuffs were made by Plauson and Vielle.<sup>27</sup> The resins used are those obtained by condensation or polymerization of phenols and aldehydes, or ketones and aldehydes. The products may be used as fat- or oil-soluble varnishes for paper, textile fabrics, leather, wood or metals, or as electrical insulators.

Kessler and Eiffaender<sup>28</sup> proposed a somewhat similar method of making an insoluble dyestuff. As an example, they mixed 60 parts of crystallized 1,4-diamino-anthraquinone with 40 parts of the condensation product of 3 parts of phenol and 1 part of acetic aldehyde and heated to about 80°C. This mass is worked on a roller mill, with the addition of 30 parts of water, until the desired degree of fineness of the coloring matter has been reached. After drying in air and grinding, the material is ready for use. It is adapted for painting on acetate silk. The condensation products of phenol sulphonic acids with formaldehyde may replace the phenol product.

A further use of dyestuffs<sup>29</sup> is the application of a dye containing a reducible CO group (bis-1,2-naphthothnophene indigo) in conjunction with a phenol-formaldehyde resin. In general, indigoid or anthraquinoid dyes are suited to the coloring of phenol-formaldehyde resins.<sup>29,2</sup>

The surfaces of hardened phenolic resins are colored blue or black by cold or slightly warm treatment first with an aqueous solution of p-phenylenediamine and then with hydrogen peroxide.<sup>28</sup>

<sup>27</sup> H. Plauson and J. A. Vielle, British P. 182,497, 1921; *J S C I*, 1921, 41, 676A. See also B. M. Lotarev, Russian P. 132, 1923; *Chem. Abs.*, 1933, 27, 4429. French P. 650,614 and 650,615, 1928, to Soc. anon pour l'ind. chim à Saint-Denis, *Chem. Abs.*, 1929, 23, 3356. H. I. Waterman, W. J. C. de Kok and A. R. Veldman, *Chem Weekblad*, 1934, 31, 608, *Brit Chem. Abs B*, 1935, 69.

<sup>28</sup> H. Kessler and L. I. Eiffaender, U. S. P. 1,892,280, Dec 27, 1932, to General Aniline Works, Inc; *Chem. Abs.*, 1933, 27, 2050.

<sup>29</sup> Swiss P. 155,711, 1931, to Soc pour l'ind. chim à Bâle. *Chem. Abs.*, 1933, 27, 1220.

<sup>29,2</sup> German P. 585,961, 1933, to Soc. pour l'ind. chim. à Bâle, *Chem. Abs.*, 1934, 28, 1560.

<sup>28</sup> German P. 581,907, 1933, to F. Raschig G.m b H., *Chem. Abs.*, 1934, 28, 1208.

## Chapter 21

### Uses of Phenol-Aldehyde Resins

#### I. Coatings

In addition to attempts to obtain oil-soluble phenol resins (see Chapter 19) which will replace natural resins in oil varnishes, investigations have been directed also to dissolving ordinary phenol resins directly in volatile solvents to form spirit-varnishes.<sup>1</sup> The difficulty has been that phenol resins in the heat-hardened stage (which is the most desirable for the final film) are insoluble in all ordinary solvents. Consequently phenol-resin spirit-varnishes must be made with the reactive type of phenol resin (resol) dissolved in a volatile solvent. Conversion to the infusible and insoluble state is effected by baking the coating.<sup>2</sup>

A varnish of this type suggested by Baekeland<sup>3</sup> consisted of an alkali-catalyzed phenol-aldehyde condensation product dissolved in a volatile solvent, e.g., alcohol or acetone. A small amount of a basic condensing agent was incorporated in the varnish to assist the transformation into an infusible form when the coating was baked. Another varnish of this type contains a mixture of a volatile solvent, e.g., acetone, and a high-boiling solvent, e.g., amyl alcohol.<sup>4</sup> A mixture of acetone and a cyclic hydrocarbon (e.g., benzene or trimethylene) is employed as the solvent in a phenol-resin spirit-varnish intended to be moisture-free.<sup>5</sup> Alcohol as a solvent was found objectionable in this case since it tends to absorb moisture from the air.

According to Jones<sup>6</sup> a varnish of good penetrating power for porous materials (wood) is obtained by dissolving a pasty phenol-aldehyde condensation product in a mixture of aniline and xylene. Another non-alcoholic varnish is made by dissolving a phenol resin in alcohol, precipitating with moisture-free turpentine and then dissolving the precipitated resin in a mixture of turpentine and amyl acetate.<sup>7</sup>

In previous chapters mention has been made of the use of hexamethylenetetramine as a hardening-agent for phenol resins. Aylsworth<sup>8</sup> suggested varnishes consisting of phenol-formaldehyde condensation products, hexamethylenetetramine or paraformaldehyde, and various solvents, including alcohol, acetone, chloro-

<sup>1</sup> Discussions of the solubility of phenol-aldehyde resins are given by A. A. Drummond, *J. Oil, Colour Chem. Assoc.*, 1925, 8, 62; 1927, 10, 83; *Chem. Abs.*, 1925, 19, 1955; 1927, 21, 2194. A. C. Hopper, *Chem. Age (London)*, 1925, 13, 370; *Chem. Abs.*, 1926, 20, 872.

<sup>2</sup> It was at one time alleged (H. von der Heyden and K. Typke, *Z. angew. Chem.*, 1925, 38, 421; *Chem. Abs.*, 1925, 19, 2277) that 15-16 per cent of the phenol resin volatilizes during the baking process. Later investigations could not confirm this. See J. Scheiber, *Z. angew. Chem.*, 1925, 38, 904; *Chem. Abs.*, 1926, 20, 117.

<sup>3</sup> L. H. Baekeland, U. S. P. 954,666, Apr. 12, 1910; *Chem. Abs.*, 1910, 4, 1689.

<sup>4</sup> L. H. Baekeland, U. S. P. 1,018,385, Feb. 20, 1912, to General Bakelite Co.; *J.S.C.I.*, 1912, 31, 347. British P. 6294, 1913; *J.S.C.I.*, 1913, 32, 298.

<sup>5</sup> L. H. Baekeland, U. S. P. 1,037,719, Sept. 3, 1912; *Chem. Abs.*, 1912, 6, 3534. British P. 6293, 1912; *J.S.C.I.*, 1913, 32, 298.

<sup>6</sup> W. B. Jones, U. S. P. 1,200,781, Oct. 10, 1916, to General Bakelite Co.; *J.S.C.I.*, 1916, 35, 1236.

<sup>7</sup> V. V. Chernov, Russian P. 13,765, 1930; *Chem. Zentr.*, 1931, 1, 3522.

<sup>8</sup> J. W. Aylsworth, U. S. P. 1,098,608, June 2, 1914, to Condensite Co. of America; *Chem. Abs.*, 1914, 8, 2815. U. S. P. 1,102,632, July 7, 1914; *Chem. Abs.*, 1914, 8, 3127. U. S. P. 1,137,374, Apr. 27, 1915; *Chem. Abs.*, 1915, 9, 1696. See also L. V. Redman, U. S. P. 1,107,708, Aug. 18, 1914; *Chem. Abs.*, 1914, 8, 3377.

naphthalene and acetylene tetrachloride. Landt and Adams<sup>9</sup> proposed to eliminate several steps in the preparation of such varnishes by synthesizing hexamethylenetetramine directly in the solvent to be employed for the varnish. One method is to react ammonia with formaldehyde in alcohol to form hexamethylenetetramine and then dissolve a phenol resin in this solution. In another procedure the resin is first dissolved in the alcohol and the hexamethylenetetramine is then produced in the solution.

To prevent the formation of bubbles in a varnish film, Cheetham<sup>10</sup> suggested the incorporation of furfural in phenol-resin varnishes of the reactive type. It was stated that the furfural tended to absorb the ammonia liberated from hexamethylenetetramine during the setting of the varnish. Other advantages reported were that furfural increases the fluidity and penetrating power of the varnish and tends to improve the gloss and elasticity of the film. Advantages in the use of furfural in phenol-resin varnishes were observed also by Redman.<sup>11</sup> The furfural was added to an aqueous alkaline solution<sup>12</sup> of a phenol-aldehyde resin to act both as a hardening agent and as a diluent for the varnish.

The statement has already been made (Chapter 15) that the alkaline-condensation of phenol and formaldehyde yields fusible and soluble resols. Careful heating of the latter converts them to resitols, which are partly soluble and are infusible but soften on heating. Further heating of resitols yields insoluble and infusible resites. These three classes, resols, resitols and resites are also designated A, B and C types, respectively, as has already been explained.

Whereas the majority of spirit-varnishes already mentioned contain resols (because of their better solubility) Elbel and Seebach<sup>13</sup> have suggested solvents for the B type (resitols) to manufacture varnishes intended to give firm and resistant films. Hydrogenated aromatic hydrocarbons, hydrogenated phenols (e.g., cyclohexanol) and cyclic ketones (e.g., cyclohexanone) were the solvents found applicable. One varnish of this type consisted of 75 parts of B stage resin dissolved in 70 parts of decahydronaphthalene and 70 parts of cyclohexanol, solution being effected by boiling under reflux. It was stated that practically the same result is obtained by dissolving a resin in the A stage in solvents of the type mentioned and then heating the solution to convert the resin to the B stage. Another modification of the procedure consists in conducting a phenol-aldehyde condensation reaction in one of the recommended solvents.<sup>14</sup>

Bender<sup>15</sup> prepared an air-drying coating composition from a resinoid made out of phenol, formaldehyde and hexamethylenetetramine. The resinoid was dehydrated and transformed to B stage by heating. The hardening reaction was arrested by addition of butyl alcohol or amyl acetate. After heating the resulting solution to complete transformation to B stage, a low-boiling alcohol or acetone was employed to achieve the desired consistency.

<sup>9</sup> G. E. Landt and W. H. Adams, Jr., U. S. P. 1,731,071 and 1,731,072, Oct. 8, 1929, to Continental Diamond Fiber Co.; *Chem. Abs.*, 1929, 23, 5600.

<sup>10</sup> H. C. Cheetham, U. S. P. 1,523,006, Mar. 3, 1925, to Bakelite Corp.; *Chem. Abs.*, 1925, 19, 1502. *British P.* 322,789, 1928; *Brit. Chem. Abs. B*, 1930, 337. *German P.* 536,677, 1928; *Chem. Abs.*, 1932, 26, 1092.

<sup>11</sup> L. V. Redman, U. S. P. 1,591,999, July 13, 1926, to Bakelite Corp.; *Chem. Abs.*, 1926, 20, 3581. *British P.* 276,417, 1926; *Chem. Abs.*, 1928, 22, 2476. *Canadian P.* 261,954, 1926; *Chem. Abs.*, 1926, 20, 3561. *German P.* 508,814, 1926; *Chem. Abs.*, 1931, 25, 634.

<sup>12</sup> See L. H. Baekeland, U. S. P. 1,085,100, Jan. 27, 1914; *Chem. Abs.*, 1914, 8, 1215.

<sup>13</sup> E. Elbel and F. Seebach, U. S. P. 1,968,440 and 1,968,441, July 31, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 6002. *British P.* 295,335, 1928 and 347,611, 1930; *Brit. Chem. Abs. B*, 1930, 469; 1931, 696. *French P.* 658,718, 1928 and its addn. 37,860, 1929; *Chem. Abs.*, 1929, 23, 5333; 1931, 25, 4724.

<sup>14</sup> E. Elbel and F. Seebach, U. S. P. 1,968,074, July 31, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 6330. See also *French P.* 725,464; 1931, to La Bakelite; *Chem. Abs.*, 1932, 26, 4969. N. I. Volunkin, *Russian P.* 4366, 1928; *Chem. Abs.*, 1928, 22, 4844.

<sup>15</sup> H. C. Bender, U. S. P. 1,922,272, Aug. 15, 1933, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 5203.

In a method employed by Shono<sup>16</sup> for manufacturing phenol-resin varnish, a phenol-aldehyde condensation is carried out first in an alkaline and then in an acid medium. The product is rapidly chilled (e.g., with ice-water) washed, dried and dissolved in equal parts of ethyl and butyl alcohols. Immediately before the solution is to be employed as a varnish, mineral acid is added to complete the final condensation.

In numerous instances, plasticizers and other synthetic resins have been used to modify the properties of phenol-resin varnishes. For instance the incorporation of dibutyl phthalate or tricresyl phosphate into such a varnish is said to improve the flexibility of the film.<sup>17</sup> Among the synthetic resins which have been incorporated with phenol-resin varnishes are the alkyd resins,<sup>18</sup> the polyvinyl esters<sup>19</sup> and the resin obtained by heating glycerol with sulphates or sulphonic acids (see Chapter 23).<sup>20</sup> Levy<sup>21</sup> has suggested the use of a varnish made by sulphonating a phenol-aldehyde resin and dissolving the resultant product in an appropriate organic solvent.

To form varnishes from insoluble or only partially soluble phenol resins, Plauson<sup>22</sup> suggested dispersing the resin in a solvent by the use of a colloid mill. The same principle was employed by Wakefield<sup>23</sup> to make a non-penetrating varnish. Rubber is reported to act as a protective colloid for stabilizing unstable suspensions consisting of a phenol-formaldehyde resin in gasoline.<sup>24</sup>

#### PHENOL RESINS IN CELLULOSE LACQUERS

In nitrocellulose and cellulose acetate lacquers a certain amount of a natural or synthetic resin is needed to offset two shortcomings, viz., lack of adhesion and lack of luster. Among the resins found useful in this way are those from phenols and aldehydes.<sup>25</sup> In selecting phenol resins for such lacquers their compatibility with cellulose esters must be considered. Hofmann<sup>26</sup> reports that in speaking of compatibility it is necessary to consider the state of affairs existing in a poly-component system. Thus, for example, one speaks of the compatibility of phenol resin with nitrocellulose in amyl acetate and not simply of the compatibility of phenol resin with nitrocellulose. It was noted that although some resins are compatible with nitrocellulose in any solvent, the majority behave differently in different solvents. The observation was also made that certain resins are compatible with nitrocellulose in some solvents only when another particular solvent is present. Clear solutions were obtained with nitrocellulose and an oil-soluble phenol resin (Amberol H-9) dissolved in amyl acetate, butyl acetate, butyl propionate or

<sup>16</sup> T. Shono, British P. 368,359, 1930, to Nippon Paint K.K.; *Brit. Chem. Abs.* B, 1932, 474. French P. 704,732, 1930; *Chem. Abs.*, 1931, 25, 4723.

<sup>17</sup> V. H. Turkington, U. S. P. 1,695,566, Dec. 18, 1928, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 1000. British P. 343,572, 1928; *Chem. Abs.*, 1931, 25, 4421. French P. 665,981, 1928; *Chem. Abs.*, 1930, 24, 1528. These plasticizers are also used to produce more flexible undercoats (G. Ebert and R. Denninger, German P. 437,102, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2317).

<sup>18</sup> W. Baird, British P. 349,464, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.* B, 1931, 728. N. Strafford and E. E. Walker, British P. 308,048, 1928, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.* B, 1929, 444. French P. 669,612, 1929; *Chem. Abs.*, 1930, 24, 1995. N. Strafford, E. E. Walker and W. J. Jenkins, British P. 312,204, 1928, to Imperial Chem. Ind.; *Brit. Chem. Abs.* B, 1929, 610. See also French P. 638,275, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 293. H. Chase, *Elec. Mfg.*, 1934, 14 (1), 23; *Chem. Abs.*, 1934, 28, 5690.

<sup>19</sup> British P. 339,271, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3581.

<sup>20</sup> S. N. Ushakov, Russian P. 23,615, 1931; *Chem. Abs.*, 1932, 26, 2073.

<sup>21</sup> L. Levy, Swiss P. 127,039, 1927; *Chem. Abs.*, 1929, 23, 1394.

<sup>22</sup> H. Plauson, U. S. P. 1,436,820, Nov. 28, 1922; *Chem. Abs.*, 1923, 17, 642. British P. 156,149, 1921; *J.S.C.I.*, 1922, 41, 381A.

<sup>23</sup> H. F. Wakefield, U. S. P. 1,756,267, Apr. 29, 1930, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 3123. See also H. W. Hutton, British P. 417,948, 1934; *Brit. Chem. Abs.* B, 1935, 34. H. C. Cheetham, U. S. P. 1,895,884, Apr. 26, 1932, to Bakelite Corp.; *Brit. Chem. Abs.* B, 1933, 277.

<sup>24</sup> R. H. Kienle, British P. 388,970, 1932, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 4431.

<sup>25</sup> See, for example, P. S. Symons, *Paint, Varnish Prod. Mgr.* 1931, 5 (4), 8; 5 (5), 5, 31.

<sup>26</sup> H. E. Hofmann, *Ind. Eng. Chem.*, 1931, 23, 127.

butyl Cellosolve. Solutions in ethyl acetate and in acetone were cleared by dilution with toluene and butyl alcohol.

According to Wilson,<sup>27</sup> the viscosity of nitrocellulose solutions can be lowered by adding a phenolic condensation product containing an active methylene compound (e.g., hexamethylenetetramine). On keeping or heating, the viscosity is further reduced.

For coating metal surfaces, Ayisworth<sup>28</sup> suggested a relatively non-inflammable varnish made from a fusible phenol (or cresol) resin and a cellulose ester dissolved in acetylene tetrachloride. Halogenated fatty acids (or their esters) can be used as plasticizers. One method of incorporating cellulose esters is to add them



Courtesy Bakelite Corp.

FIG. 73.—Rolls of Paper or Fabric Pass through a Resinoid Varnish Bath.

to the mixture of phenol and formaldehyde prior to condensation.<sup>29</sup> When phenol-formaldehyde condensation products are incorporated with nitrocellulose, cellulose acetate or other added materials,<sup>30</sup> the presence of alkaline-earth bases or alkali cyanides as catalysts causes the formation of an infusible, insoluble and acid- and alkali-resistant varnish when heated in air at 100°C.<sup>31</sup> Phenol-aldehyde lacquers have been made with such esters as cellulose acetate, formate, propionate and butyrate and with methyl and ethyl cellulose ethers.<sup>32</sup> Among the solvents employed are acetone, benzene, toluene, xylene and ethyl acetate.<sup>33</sup> A ketone-phenol-aldehyde resin<sup>34</sup> may replace the phenol-aldehyde body.<sup>35</sup> For this type

<sup>27</sup> W. C. Wilson, U. S. P. 1,795,918, Mar. 10, 1931, to John S. Stokes; *Chem. Abs.*, 1931, 25, 2581.

<sup>28</sup> J. W. Ayisworth, U. S. P. 1,094,830, Apr. 28, 1914, to Condensite Co. of America; *Chem. Abs.*, 1914, 8, 2268.

<sup>29</sup> W. B. Jones, U. S. P. 1,209,165, Dec. 19, 1916, to General Bakelite Co.; *Chem. Abs.*, 1917, 11, 710.

<sup>30</sup> M. Warchavsky, French P. 495,021, 1910.

<sup>31</sup> See L. A. Jaloustre, Z. Kheifitz and M. Warchavsky, British P. 138,061 and 139,147, 1919; *J.S.C.I.*, 1921, 40, 122A. See also Chapter 16.

<sup>32</sup> W. H. Moss, British P. 296,675, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1929, 23, 2585. Canadian P. 307,589, 1931, to H. Dreyfus; *Chem. Abs.*, 1931, 25, 1108. W. H. Moss and B. B. White, British P. 312,133, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1930, 726.

<sup>33</sup> Modifications are obtained by incorporating other materials. See German P. 554,932, 1927, to Degronite-Werke G.m.b.H.; *Chem. Abs.*, 1932, 26, 6164. G. S. Petrov, Russian P. 28,603, 1933; *Chem. Abs.*, 1934, 28, 3605.

<sup>34</sup> W. H. Moss, U. S. P. 1,929,559, Oct. 10, 1933, to Celanese Corp.; *Chem. Abs.*, 1934, 28, 80. U. S. P. 1,878,249, Sept. 20, 1932; *Chem. Abs.*, 1933, 27, 435. British P. 299,065, 1928, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1930, 333. See also Chapter 18.

<sup>35</sup> W. H. Moss, British P. 299,781 and 299,783, 1927, to British Celanese, Ltd.; *Chem. Abs.*, 1929, 23, 2688.

of coating, a mixture of a hydrocarbon, an unsaturated hydrocarbon halide and an alcohol serves as the solvent. Naphthalene, diethyl phthalate, triphenyl or tricresyl phosphate, triacetin and thiocarbanilide are suggested plasticizers.<sup>35</sup> For lacquers intended to give light-resistant coatings, Moss<sup>37</sup> has advocated the incorporation of phenol-furfural or ketone-furfural resins in nitrocellulose or cellulose acetate.

The condensation product of formalglycerol with a hydroxybenzyl alcohol is contained in a cellulose acetate lacquer suggested by Seymour.<sup>38</sup> Brushing lacquers have been made which consist essentially of a cyclohexanone-phenol-aldehyde resin, low-viscosity cellulose nitrate, ether, ethyl alcohol and the monoalkyl ether or ester of a glycol.<sup>39a</sup>

An adherent coating composition<sup>38</sup> can be made by mixing cotton flock or  $\alpha$ -cellulose with a plasticized phenol-formaldehyde resin. The reaction product of phenol, tung oil and formaldehyde, admixed with cellulose acetate or formate or with benzyl cellulose, yields another coating composition.<sup>40</sup> Shellac or other natural resins may be added to the product obtained to increase its efficiency as a sheet veneer. A similar coating comprises ripened cellulose acetate, a phenol resin (Novolak) and acetone and ethyl alcohol as solvents.<sup>41</sup> No halogenated hydrocarbons are needed as solvents in this lacquer. A varnish proposed by Frederic<sup>42</sup> contains a mixture of natural resins, phenol-aldehyde resin, collodion, powdered mica and alcohol. Before applying lacquers containing cellulose ester, the surface can be primed with a lacquer containing a phenol-formaldehyde condensation product and an alkyd resin.<sup>43</sup> The addition of an acid catalyst is sometimes required. To make a nitrocellulose or cellulose acetate film relatively fire-proof, the application of a phenol-aldehyde coating has been suggested.<sup>44</sup>

To form a polishing composition for cellulose lacquer surfaces one proposal consists in mixing together a cellulose ester, a phenol-aldehyde resin, benzene, ethyl phthalate (plasticizer) and an abrasive.<sup>45</sup>

The suggestion has often been made to employ resin-modified cellulose lacquers as insulating-coatings. For instance, Hull<sup>46</sup> covered wires with a composition containing cellulose acetate (30 parts), a phenol resin (10 parts) and furfural (300 parts). For a similar purpose Schnable<sup>47</sup> employed a cellulose acetate-phenol resin lacquer and then applied as an outer coating a mixture of ozokerite and castor oil. The laminated insulation thus formed was subjected to a baking treat-

<sup>35</sup> C. Dreyfus, U. S. P. 1,909,935, May 23, 1933; *Chem. Abs.*, 1933, 27, 4108. W. H. Moss, British P. 301,497, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1929, 23, 4071.

<sup>37</sup> W. H. Moss and B. B. White, U. S. P. 1,902,255, Mar. 21, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 3350. U. S. P. 1,941,708, Jan. 2, 1934, *Chem. Abs.*, 1934, 28, 1879. Canadian P. 329,708, 329,709 and 329,710, 1933, to C. Dreyfus, *Chem. Abs.*, 1933, 27, 2051. W. H. Moss, British P. 307,280 and 307,291, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs. B.*, 1930, 469.

<sup>38</sup> G. W. Seymour, U. S. P. 1,828,449, Oct. 20, 1931, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 1460. Canadian P. 317,117, 1931, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 1460.

<sup>39a</sup> H. Finkelstein, U. S. P. 1,818,547, Aug. 11, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 518. U. S. P. 1,812,145, June 30, 1931; *Chem. Abs.*, 1931, 25, 5048. U. S. P. 1,801,340 and 1,801,341, Apr. 21, 1931; *Chem. Abs.*, 1931, 25, 3502. See also G. Steimmig, U. S. P. 1,883,060, Oct. 18, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 857.

<sup>40</sup> F. Groff, U. S. P. 1,885,028, July 5, 1932, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 4487. British P. 358,120, 1930; *Brit. Chem. Abs. B.*, 1931, 1147. French P. 702,090, 1930; *Chem. Abs.*, 1931, 25, 4138.

<sup>41</sup> V. H. Turkington, U. S. P. 1,954,836, Apr. 17, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 3921. British P. 342,286, 1929; *Chem. Abs.*, 1931, 25, 4421. French P. 684,747, 1929; *Chem. Abs.*, 1930, 24, 5517. Canadian P. 317,205, 1931; *Chem. Abs.*, 1932, 26, 1460.

<sup>42</sup> German P. 536,372, 1928, to Firma Louis-Blumer; *Chem. Abs.*, 1932, 26, 1143.

<sup>43</sup> L. C. Frederic, French P. 622,299, 1928; *Kunststoffe*, 1928, 18, 72.

<sup>44</sup> N. Strafford, E. E. Walker and W. J. Jenkins, British P. 312,204, 1928, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B.*, 1929, 610. See also British P. 298,616, 1928, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B.*, 1930, 337. French P. 669,290, 1929; *Chem. Abs.*, 1930, 24, 1753.

<sup>45</sup> H. W. Matheson, U. S. P. 1,809,581, July 8, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1919, 13, 2278. W. A. Beatty, U. S. P. 1,153,963, Nov. 2, 1915; *Chem. Abs.*, 1916, 10, 158. Cf. C. Dreyfus, British P. 316,984, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 1996.

<sup>46</sup> British P. 352,547, 1930, to British Celanese, Ltd.; *Brit. Chem. Abs. B.*, 1931, 895.

<sup>47</sup> S. M. Hull, U. S. P. 1,697,870, Jan. 8, 1929, to Western Electric Co.; *Chem. Abs.*, 1929, 23, 1191.

<sup>48</sup> G. L. Schnable, U. S. P. 1,720,749, July 16, 1929, to Western Electric Co.; *Chem. Abs.*, 1929, 23, 4283.

ment. A wire enamel suggested by Ehrenzweig<sup>44</sup> contains phenol-aldehyde resin (A stage), tolyl phosphate, turpentine, dicresylin and a cellulose ester.

#### APPLICATIONS OF PHENOL-RESIN SOLUTIONS

Numerous proposals have been made for the use of phenol-resin varnishes in all types of protective coatings, particularly for metals.<sup>45</sup> In addition, these solutions have been employed to impregnate paper and fabrics for insulating-media and for the manufacture of laminated boards and gears (see Chapter 22).

In applying a phenol-aldehyde resin coating to metal one of the chief points of interest is the acid- and corrosion-resistance of the finished material.<sup>50</sup> A study of the factors influencing the chemical resistance of phenol-aldehyde resins has been made by Sokolov.<sup>51</sup> This work reveals that the time-duration and temperature of condensation determine very slightly the ability of the ultimate resin to withstand chemical action. However, the type of condensing agent is an unimportant factor, provided it is present in proportions of not more than 10 per cent. When more than this amount of condensing agent is used, the resulting resin is more hygroscopic and offers less resistance to dilute acids. Resistance to chemical reagents is lowered by: (1) acid condensing agents (even when neutralized later); (2) the presence of alcohol; (3) decreasing the proportion of formaldehyde in the reaction mixture.

One of the earliest uses suggested for phenol resin solutions was the coating of the inside of metal food-containers.<sup>52</sup> Investigations have shown that a film of phenol resin on a metallic container prevents the catalytic effect of the metal in promoting rancidity of fats stored in the container.<sup>53</sup>

The protection afforded against fatty acids has suggested the use of phenol resin to coat metallic filter cloths apt to come in contact with such acids.<sup>54</sup>

In most instances it is important that a coating should adhere well to the surface covered, so that vibrations of any sort will not endanger the protective action.<sup>55</sup> It has been reported that hammer-proof and acid-proof coating for steel pipe is obtained by pickling the surface before dipping the pipe in the phenol resin solution.<sup>56</sup> Phenol reacts with easily oxidizable metals, producing a surface to which a lacquer can cling tenaciously. Michel<sup>57</sup> made use of this principle by incorporating an excess of phenol in a phenol-resin varnish intended for metals. Jones<sup>58</sup> suggested an undercoat of a linseed oil varnish to secure good adherence of phenol-aldehyde films. Another proposal is to etch a metallic surface with magnesium chloride solution. Any magnesium chloride adhering to the surface is con-

<sup>44</sup> A. Ehrenzweig, British P. 355,730, 1931; *Brit. Chem. Abs.* B, 1933, 199. British P. 386,102, 1933; *Chem. Abs.*, 1933, 27, 5447. French P. 728,149, 1931; *Chem. Abs.*, 1932, 26, 5777.

<sup>45</sup> Cf. H. Lebach, *Z. angew. Chem.*, 1925, 38, 1091; *Chem. Abs.*, 1926, 20, 1497. A. E. Dawkins, P. R. Weldon and W. H. Summers, *Commonwealth Australia Munitions Supply Board, Tech. Repts.*, 1921-2, 14; *Chem. Abs.*, 1924, 18, 598. British P. 258,908, 1926, to International Gen. Electric Co.; *Brit. Chem. Abs.* B, 1927, 767. F. E. Payne, British P. 322,694, 1929; *Chem. Abs.*, 1930, 24, 2816. J. A. Steurer, U. S. P. 1,459,803, June 26, 1923; *Chem. Abs.*, 1923, 17, 2941. H. Inoue and S. Haga, Japanese P. 91,890, 1931; *Chem. Abs.*, 1932, 26, 1923. British P. 262,824, 1926, to Soc. anon. des manuf. des glaces et prod. chim. de St. Gobain, Chauný et Cirey; *Brit. Chem. Abs.* B, 1927, 702.

<sup>46</sup> See S. U. Davuidov, *Lesokhim Prom.*, 1932, 1, (5-6), 36; *Chem. Abs.*, 1933, 27, 5508.

<sup>47</sup> A. D. Sokolov, *Plast. Massu*, 1933, (3), 1; *Chimie et industrie*, 1934, 31, 657; *Chem. Abs.*, 1934, 28, 3008.

<sup>48</sup> L. H. Baekeland, U. S. P. 957,137, May 3, 1910.

<sup>49</sup> J. A. Emery and R. R. Henley, *Ind. Eng. Chem.*, 1922, 14, 937.

<sup>50</sup> E. J. Sweetland, F. W. Manning and W. S. Hilpert, U. S. P. 1,292,535, Jan. 28, 1919, to E. J. Sweetland; *Chem. Abs.*, 1919, 13, 920.

<sup>51</sup> This is particularly true in the case of coatings for aircraft. See J. L. McCloud, *Ind. Eng. Chem.*, 1931, 23, 1324.

<sup>52</sup> Report of W. Trinks, *Iron Age*, 1929, 124, 1518. See also Mauermann, *Schweiz. Ver. Gas Wasserf. Monats.-Bull.*, 1933, 12, 73; *Chem. Abs.*, 1933, 26, 4160.

<sup>53</sup> G. Michel, Canadian P. 235,118, 1928; *Chem. Abs.*, 1929, 23, 990.

<sup>54</sup> W. B. Jones, U. S. P. 1,171,725, Feb. 15, 1916; *Chem. Abs.*, 1916, 10, 1104.



verted into magnesium hydroxide and oxide. Then a solution of phenol and formaldehyde is applied and changed into an insoluble resin by heat.<sup>60</sup>

In order to secure good adhesion of phenol resin coatings on metals, Townsend<sup>60</sup> recommended that the surface be coated with a thin film of another metal. This is accomplished by employing a solution of a metal lower in the electromotive-force series than the metal to be coated. Thus iron is given a coating of copper by applying copper chloride solution. In the method suggested, a varnish is prepared by dissolving cupric chloride and a phenol-aldehyde resin in methyl or ethyl alcohol.<sup>61</sup>

Baekeland<sup>62</sup> stated that lack of adherence of phenol resin coatings is caused by a slight shrinkage during the hardening process. He suggested the inclusion of finely divided inert material (e.g., asbestos, clay, sand) to minimize the contraction of the film.

A great number of the proposed phenol-resin coatings for metals contain inert material for various reasons. For example, in coating aluminum parts for automobiles, the metal pores should be sealed according to Peterson.<sup>63</sup> This purpose is accomplished by a phenol-formaldehyde resin mixture containing 10 per cent of aluminum silicate. Aluminum may also be protected by using an undercoat of wax and a final coating of resin. The wax is volatilized and coating burned into the metal by heating to 250-400°C.<sup>64</sup> A primer containing titanium dioxide and a phenolic resin has been found to be good for magnesium alloys.<sup>65</sup>

To produce a finish of enamel-like character, a liquid phenol-formaldehyde condensation product is mixed with sodium silicate, casein waste being added as a protective colloid to prevent precipitation of silicic acid.<sup>66</sup> An enamel which dries at ordinary temperatures to form a hard film contains a phenol resin, hydrochloric acid as a hardening agent and powdered talc as a filler.<sup>67</sup>

In covering metals with phenol-aldehyde resins, Kränzlein and Müller<sup>68</sup> employed two or more layers of material. The underlying coat contained relatively soft filling materials (e.g., graphite, talc, asbestos) to impart flexibility. The top layer consisted of a phenol resin solution to which hard filling materials (e.g., silicon, quartz) had been added to give the coating mechanical and chemical resistance. In another proposal the preliminary coat consisted of an anti-corrosive paint, the second a casein paint and the final coating was a fusible phenol resin.<sup>69</sup>

Wirth<sup>70</sup> coated metals with a layer of phenol-aldehyde resin, followed by a sheet of asbestos. After this had been hardened with heat another coating of phenol resin was applied to the asbestos and also heat-hardened. Instead of applying the layer of inert material in sheet form, the asbestos may be mixed with the first

<sup>60</sup> German P. 382,749, 1920, to Ges. für Technik m.b.H.; *J.S.C.I.*, 1924, 43, 104B.

<sup>61</sup> C. P. Townsend, U. S. P. 1,146,214, July 13, 1915; *Chem. Abs.*, 1915, 9, 2432.

<sup>62</sup> Still another method of securing adhesion is to provide the surface of the metal with notches or recesses to which the coating can cling. See British P. 250,325, 1925, to Säureschutz G.m.b.H.; *Brit. Chem. Abs. B.*, 1927, 147.

<sup>63</sup> L. H. Baekeland, U. S. P. 932,230, Jan. 24, 1911. See also *Chem. Met. Eng.*, 1912, 10, 53.

<sup>64</sup> W. C. Peterson, U. S. P. 1,673,280, June 5, 1928, to Packard Motor Co.; *Brit. Chem. Abs. B.*, 1928, 575.

<sup>65</sup> Swiss P. 159,677, 1933, to Sigg A.-G.; *Chem. Abs.*, 1934, 28, 663.

<sup>66</sup> F. Kolke, *Farben-Ztg.*, 1933, 38, 1756; *Chem. Abs.*, 1934, 28, 1875.

<sup>67</sup> A. Jaeger, U. S. P. 1,830,906, Nov. 10, 1931, to Herold A.-G.; *Chem. Abs.*, 1932, 26, 861. German P. 534,659, 1927; *Chem. Abs.*, 1932, 26, 1460.

<sup>68</sup> British P. 215,722, 1924, to Soc. anon. dite Progil; *J.S.C.I.*, 1925, 44, 107B. Other fillers include china clay, chalk and graphite. See French P. 745,250, 1933, to Metallisierungs-G.m.b.H.; *Chem. Abs.*, 1933, 27, 4427.

<sup>69</sup> G. Kränzlein and R. K. Müller, U. S. P. 1,873,945, Aug. 23, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 6164. British P. 380,944, 1930; *Brit. Chem. Abs. B.*, 1932, 235. French P. 720,136, 1931; *Chem. Abs.*, 1932, 26, 3943. German P. 497,056, 1930; *Chem. Abs.*, 1930, 24, 3662. German P. 600,891, 1934; *Chem. Abs.*, 1934, 28, 6581.

<sup>70</sup> E. Asser, British P. 389,411, 1932, to G. Ruth A.-G.; *Brit. Chem. Abs. B.*, 1933, 309.

<sup>71</sup> J. K. Wirth, U. S. P. 1,533,566, April 27, 1926; *Chem. Abs.*, 1926, 20, 2053. British P. 171,369 and 183,187, 1921; *Chem. Abs.*, 1923, 16, 995; 1923, 17, 2411.

coating of phenol resin.<sup>71</sup> It is stated that coatings built up in this manner with alternate layers of phenol resin and of a phenol resin-inert filler mixture are readily repaired in case of damage, since fresh applications of resin will adhere easily to the rough intermediate layers.<sup>72</sup>

When mixed with the proper filling materials (graphite, silica, etc.) phenol-resin coatings have found use in containers for hydrofluoric acid,<sup>73</sup> sulphur chloride<sup>74</sup> and luminescent paints.<sup>75</sup> An impervious coating composition for metals, as proposed by White,<sup>76</sup> consists of a mixture of phenol resin, rubber and sulphur in aqueous dispersion. The preparation of lacquers comprising phenol-aldehyde condensates (or other synthetic resins) and carbon black is described by Wiegand.<sup>77</sup>

For accelerating the hardening of phenol-aldehyde resin coatings, certain metallic oxides (lead dioxide or manganese dioxide) have been suggested.<sup>78</sup> Silicon and graphite are incorporated to increase acid-resistance. An acid-resistant coating composition used by Klas<sup>79</sup> consists of a tar-oil solution of phenol resin to which finely powdered quartz has been added. The metal to be coated is heated to a high temperature before the composition is applied, thereby facilitating the hardening process. To eliminate bubbling and blistering when coatings are thus applied, small amounts of acetic acid, cresol or glycerol are said to be effective.<sup>80</sup>

Phenol-resin solutions have found some application as insulating-varnishes, particularly as coatings for electric condensers. This is of course simply a variation in the employment of phenol resins for insulation as described in Chapter 22. One varnish of this type consists of a mixture of a phenol-aldehyde resin in alcohol with paraffin oil in amyl acetate. The coating dries to a rubber-like consistency.<sup>81</sup> Another coating for condensers consists of successive layers of shellac and phenol resin.<sup>82</sup> In coating electric condensers with phenol-aldehyde resins, Kempton<sup>83</sup> suggested that the hardening be carried out in several stages of alternate heating and cooling, to prevent damage to the condenser laminations. An electrical resistor may be made by applying a mixture of phenol resin and graphite to a fibrous strip.<sup>84</sup> Dumert<sup>85</sup> employed a different procedure by utilizing a colloidal mixture of graphite and resin on a rod of insulating material. The coating was hardened by heating at 150°C.

Baekeland and Thurlow<sup>86</sup> proposed the use of phenol-aldehyde resin solutions as coating compositions for wood. After the coating has been applied, the surface of the wood is pressed against a smooth metal sheet heated to the proper tem-

<sup>71</sup> J. K. Wirth, U. S. P. 1,767,421, June 24, 1930; *Chem. Abs.*, 1930, 24, 4363. British P. 292,334, 1927; *Brit. Chem. Abs. B*, 1928, 606.

<sup>72</sup> British P. 253,531, 1925, to C. ten Doornkaat-Koolman; *Brit. Chem. Abs. B*, 1927, 260.

<sup>73</sup> British P. 233,868, 1927, to Traun & Söhne, vorm Harburger Gummikamm-Compagnie; *Chem. Abs.*, 1928, 22, 4210.

<sup>74</sup> R. Dittmar, *Gumma-Ztg.*, 1927, 41, 1348; *Chem. Abs.*, 1927, 21, 2076. See also M. U. Borodulin and R. G. Belozerskaya, *Trans. State Inst. Applied Chem. (Leningrad)*, 1932, 15, 87; *Chem. Abs.*, 1933, 27, 2827.

<sup>75</sup> M. de Lesnieres, French P. 655,265, 1927; *Chem. Abs.*, 1929, 23, 4089. For making of luminescent paints from phenolic resins see L. C. F. Pechin, French P. 693,844, 1930; *Chem. Abs.*, 1931, 25, 1692.

<sup>76</sup> E. E. White, British P. 217,350, 1928, to Dunlop Rubber Co.; *Brit. Chem. Abs. B*, 1929, 863.

<sup>77</sup> W. B. Wiegand, British P. 418,080, 1934; *Chem. Abs.*, 1935, 29, 1665.

<sup>78</sup> K. Diets, K. Frank, F. Privinsky and E. Thiel, German P. 595,014 and 595,233, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 4257, 4258.

<sup>79</sup> H. Klas, U. S. P. 1,932,699, Oct. 31, 1933, to Vereinigte Stahlwerke A.-G.; *Chem. Abs.*, 1934, 28, 461. German P. 595,466, 1934; *Chem. Abs.*, 1934, 28, 4030. British P. 348,338, 1931; *Brit. Chem. Abs. B*, 1932, 473.

<sup>80</sup> British P. 337,192 and 338,983, 1929, to Herold A.-G.; *Chem. Abs.*, 1931, 25, 2012, 2581.

<sup>81</sup> J. L. R. Hayden, U. S. P. 1,096,539, May 19, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 2312.

<sup>82</sup> British P. 276,635, 1926, to R. Bosch, A.-G.; *Chem. Abs.*, 1928, 22, 2475.

<sup>83</sup> W. H. Kempton, U. S. P. 1,249,770, Dec. 11, 1917, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1918, 12, 337.

<sup>84</sup> L. L. Howard and A. H. Haroldson, U. S. P. 1,910,391, May 25, 1933, to Continental Diamond Fibre Co.; *Brit. Chem. Abs. B*, 1934, 285.

<sup>85</sup> V. Dumert, *Nature*, 1933, 132, 1008; *Brit. Chem. Abs. A*, 1934, 164.

<sup>86</sup> L. H. Baekeland and N. Thurlow, U. S. P. 1,019,408, Mar. 5, 1912, to General Bakelite Co.; *Chem. Abs.*, 1912, 6, 1377.

perature to harden the resin. If a decorative effect is desired, the metal sheet is provided with an embossed design. During the baking of resin-coated wood, blistering of the film may occur from the expansion of air and water vapor in the pores of the wood. To avoid this, Aylsworth<sup>87</sup> heated the wood for several hours at 105-120°C. and then applied the coating while the article was still hot. Essentially the same purpose was accomplished by Buffum<sup>88</sup> by coating wood with molten rosin to expel air and moisture. The subsequent layer of phenol resin was then hardened at a temperature below the melting point of rosin. The statement has been made by Hunt<sup>89</sup> that phenol-resin varnishes are superior to ordinary spar varnishes in retarding moisture changes in wood. No material has yet been found which will entirely prevent such changes. For making wooden rollers, bobbins and poles used in textile industry water- and acid-proof, water and air in the wood are first removed by treatment with alcohol. The phenol-formaldehyde coating composition is then applied and stoved at 150°C.<sup>90</sup> A method that differs somewhat from the above procedures consisted of partially polymerizing a preliminary coating at 40-50°C., applying a second coat and then changing to the infusible state by heating to 140-150°C. This process is reported to give a durable acid-proof surface.<sup>91</sup>

By grinding a natural gum (gum arabic or tragacanth) with a fusible phenol resin in a colloid mill, Tuchfarber<sup>92</sup> obtained an aqueous dispersion to be applied to wood as an undercoating for ordinary varnish or lacquer. It was stated that this treatment imparted a decorative finish and at the same time rendered the wood impervious to moisture.

To prevent discoloration of ebonite panels by the action of light, a coating of phenol-aldehyde resin has been proposed.<sup>93</sup> Layers of this resin are applied to concrete to render it impervious to water and oils.<sup>94</sup> By incorporating various toxic materials in phenol-aldehyde resin solutions, anti-fouling paints are obtained.<sup>95</sup> The toxic agents include phenol, cacodylic acid and salts of copper, mercury and arsenic. Anti-fouling varnishes are employed principally to prevent barnacles and fungous growths from accumulating on structures submerged in sea water.<sup>96</sup>

Solutions of phenol resins have been suggested for impregnating paper to give it transparency.<sup>97</sup> Such material is intended for photographic films and for trans-

<sup>87</sup> J. W. Aylsworth, U. S. P. 1,139,470, May 18, 1915, to Condensite Co. of America; *Chem. Abs.*, 1915, 9, 1849.

<sup>88</sup> E. S. Buffum, U. S. P. 1,197,601, Sept. 12, 1916; *J.S.C.I.*, 1916, 35, 1123.

<sup>89</sup> G. M. Hunt, *Circ. U. S. Dept. Agr.*, 1930, 128, 1, *Chem. Abs.*, 1931, 25, 4378. See also F. G. Browne, *Ind. Eng. Chem.*, 1933, 25, 835.

<sup>90</sup> T. Wareing, British P. 384,369, 1932; *Chem. Abs.*, 1933, 27, 5510.

<sup>91</sup> P. A. Issunskii, *Lesokhim. Prom.*, 1932, 1 (3), 3; 1 (4), 6, *Chem. Abs.*, 1933, 27, 5508.

<sup>92</sup> F. Tuchfarber, U. S. P. 1,972,502, Sept. 4, 1934, to R. W. Callaway and A. N. Mann; *Chem. Abs.*, 1934, 28, 6546.

<sup>93</sup> P. E. Wells, British P. 303,814, 1927, to British Hard Rubber Co., Ltd; *Chem. Abs.*, 1929, 23, 4542.

<sup>94</sup> L. H. Bakeland, U. S. P. 1,160,363, Nov. 16, 1915, to General Bakelite Co.; *Chem. Abs.*, 1916, 10, 263. J. Marcussou, U. S. P. 1,521,384, Dec. 30, 1924; *Chem. Abs.*, 1925, 19, 715. A. Kneip, U. S. P. 1,965,248, July 3, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5612. British P. 376,047, 1931; *Brit. Chem. Abs. B.*, 1932, 902. French P. 686,705, 1929, to Etablissements Brisset & Sanna; *Chem. Abs.*, 1931, 25, 792. A phenol-formaldehyde coating has been used to preserve fossil bones (*J.S.C.I.*, 1933, 52, 147).

<sup>95</sup> Carleton Ellis, U. S. P. 994,420, Dec. 28, 1909, to Ellis-Foster Co.; *Chem. Abs.*, 1910, 4, 681. A. P. Horn, U. S. P. 898,476, Sept. 15, 1908; *Chem. Abs.*, 1909, 3, 383. L. Collardou, U. S. P. 1,105,619, Aug. 4, 1914; *Chem. Abs.*, 1914, 8, 3244. British P. 9040, 1913; *Chem. Abs.*, 1914, 8, 3377. German P. 274,875, 1913; *Chem. Abs.*, 1914, 8, 3378. French P. 453,395, 1913; *Chem. Abs.*, 1914, 8, 365. A. Heilmann, U. S. P. 1,176,056, Mar. 21, 1916; *J.S.C.I.*, 1916, 35, 556. British P. 11,394, 1914; *J.S.C.I.*, 1915, 34, 815. C. P. Townsend, U. S. P. 1,273,984, July 30, 1918, to General Bakelite Co.; *J.S.C.I.*, 1918, 37, 663A.

<sup>96</sup> An analogous application is the use of phenol resin solutions as insecticides. See R. Falek, German P. 365,745, 1919; *J.S.C.I.*, 1923, 42, 326A. German P. 384,354, 1920, to F. Raschig, Chem. Fabr.; *J.S.C.I.*, 1924, 43, 442B. F. Wolff, German P. 492,463, 1928; *Chem. Abs.*, 1930, 24, 2828. German P. 337,061, 1910, to Holzverkohlungs-Ind. A.-G.; *J.S.C.I.*, 1921, 40, 602A.

<sup>97</sup> H. Gessell, U. S. P. 1,377,904, Sept. 3, 1918; *Chem. Abs.*, 1918, 12, 2440. F. K. Wickel, British P. 229,161, 1924; *Chem. Abs.*, 1925, 19, 8018. French P. 631,645, 1926; *Brit. Chem. Abs. B.*, 1930, 279. V. Bausch, U. S. P. 1,787,564, Jan. 6, 1931; *Chem. Abs.*, 1931, 25, 653. British P. 260,306, 1929, to F.

parent wrappings. Coating viscose films (Cellophane) with a phenol resin is said to improve heat- and moisture-resistance and to increase the dielectric strength.<sup>106</sup> Films of cellulose esters, coated with phenol resin, were employed by Drew<sup>99</sup> as packaging material. A stencil sheet suggested by Horii<sup>100</sup> consists of yoshino paper impregnated with a solution of phenol-aldehyde resin, nitrocellulose, stearin and castor oil in alcohol or amyl acetate. Another coating composition for stencil paper proposed by Carr<sup>101</sup> contains 10 parts of a 45 per cent solution of a phenol-formaldehyde resin, 2 of aluminum stearate, 14 of chlorinated rubber and 13 of corn oil.

Transfer paper (for imprinting decorative designs on various objects) can be made by coating paper with a phenol-aldehyde resin, a fusible wax, vegetable oils and pigments.<sup>102</sup> Cellulose acetate may also be added to these coating compositions.<sup>103</sup> A carbon paper has been made by applying a mixture of purple lake, china clay, a phenol-aldehyde resol, cyclohexanol, acetone and methylated spirit to a carrier sheet.<sup>104</sup>

Insulating sheets may be formed from threads of spun paper after impregnation with a binder consisting of a phenol-aldehyde resin.<sup>105</sup> Waterproofed fiber tubes have been made by filling the pores with sulphur and coating with a phenol-formaldehyde resin.<sup>106</sup>

The principal outlet for fabrics impregnated with phenol resins is in the manufacture of laminated articles (see Chapter 22). To some extent resin-coated fabrics find other uses. For instance, fabrics for aircraft (e.g., balloons) have been impregnated with phenol resin to render them impervious to gases.<sup>107</sup>

To make fabrics crease-proof it has been suggested that they be coated or impregnated with a solution of a phenol resin.<sup>108</sup> The properties of fabrics are said to be improved by treatment with solutions of phenol resin and salts of aluminum, zirconium, tin or zinc.<sup>109</sup> Phenolic coating compositions are said to make cloth waterproof.<sup>110</sup> Aqueous solutions of phenol resin have been employed by Hochstetter<sup>111</sup> to make cloth flameproof. Other related uses for phenol-aldehyde

Schoeller and Bausch; *Brit. Chem. Abs. B*, 1927, 621. R. Berthon, U. S. P. 1,707,157, Mar. 26, 1929; *Chem. Abs.*, 1929, 23, 2113.

<sup>99</sup> H. L. Bender, British P. 355,318, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 1006. French P. 695,589, 1930; *Chem. Abs.*, 1931, 25, 2822.

<sup>100</sup> R. G. Drew, British P. 405,247, 1934, to Minnesota Mining & Mfg. Co.; *Chem. Abs.*, 1934, 28, 4191.

<sup>101</sup> S. Horii, U. S. P. 1,698,705, Jan. 8, 1929; *Brit. Chem. Abs. B*, 1929, 320. See also British P. 352,460, 1930, to Ditto, Inc.; *Chem. Abs.*, 1932, 26, 4145.

<sup>102</sup> K. W. Carr, U. S. P. 1,916,203, July 4, 1933, to Ditto, Inc.; *Chem. Abs.*, 1933, 27, 4641. U. S. P. 1,894,731, Jan. 17, 1933; *Chem. Abs.*, 1933, 27, 2543.

<sup>103</sup> W. S. Lawrence, U. S. P. 1,827,591, Oct. 13, 1931, to Kaumagraph Co.; *Chem. Abs.*, 1932, 26, 605. U. S. P. 1,977,680, Oct. 23, 1934; *Chem. Abs.*, 1935, 29, 258. British P. 331,135, 1929; *Chem. Abs.*, 1930, 24, 6040.

<sup>104</sup> W. S. Lawrence, U. S. P. 1,954,878, Apr. 17, 1934, to Kaumagraph Co.; *Chem. Abs.*, 1934, 28, 3911.

<sup>105</sup> R. D. Main and E. G. Nixon, British P. 295,118 and 295,119, 1927, to Lamson-Paragon Supply Co., Ltd.; *Brit. Chem. Abs. B*, 1928, 744.

<sup>106</sup> Allgemeine Elektrizitäts-Ges., British P. 341,535, 1928, to International General Electric Co.; *Chem. Abs.*, 1933, 27, 544.

<sup>107</sup> F. A. Burningham, G. A. Richter, W. B. Van Arsdell and D. B. White, U. S. P. 1,396,021, Nov. 28, 1921, to Brown Co.; *Chem. Abs.*, 1922, 16, 647.

<sup>108</sup> K. Huertle, U. S. P. 1,763,586, June 10, 1930, to Goodyear-Zeppelin Corp.; *Chem. Abs.*, 1930, 24, 2912. British P. 304,775, 1928; *Chem. Abs.*, 1929, 23, 4836. See also A. S. Gregg, British P. 300,357, 1927; *Chem. Abs.*, 1929, 23, 4103. One method of impregnating fabrics with phenol resin is described by N. S. Clay, U. S. P. 1,519,239, Dec. 16, 1924, to Westinghouse Elec. & Mfg. Co.

<sup>109</sup> R. P. Foulds, J. Marsh and F. C. Wood, U. S. P. 1,734,516, Nov. 5, 1929, to Tootal Broadhurst Lee Company, Ltd.; *Chem. Abs.*, 1930, 24, 511. R. P. Foulds, J. T. Marsh, F. C. Wood, H. Boffey and J. Tankard, British P. 291,473, 1926, to Tootal Broadhurst Lee Company, Ltd.; *Chem. Abs.*, 1929, 23, 1289. German P. 499,818, 1930; *Chem. Abs.*, 1930, 24, 4643.

<sup>110</sup> British P. 413,828, 1933, to Heberlein Co. A.-G.; *Brit. Chem. Abs. B*, 1934, 831. French P. 749,117, 1933; *Chem. Abs.*, 1934, 28, 842.

<sup>111</sup> British P. 887,125, 1932, to Johnson & Johnson, Ltd.; *Brit. Chem. Abs. B*, 1933, 345.

<sup>112</sup> F. W. Hochstetter, U. S. P. 1,961,043, May 29, 1934, to Treedale Laboratories, Inc.; *Chem. Abs.*, 1934, 28, 4612.

resins include treatment of gut for tennis rackets<sup>112</sup> and impregnation of fabrics for rubber-coated tires.<sup>113</sup>

Artificial leather has been fabricated from interfelted cellulose fiber by saturation with an aqueous dispersion of rubber, drying and then impregnating with a phenol-formaldehyde resin. The final product is duly obtained by curing at elevated temperature.<sup>114</sup> Leather coated with phenol-formaldehyde resins resists water-penetration but tends to be brittle.<sup>115</sup> DeVries<sup>116</sup> suggested that a coating composition containing phenolic resin be used for coating rubber or rubber-surfaced fabrics.

In preparing a substitute for glass, Moss<sup>117</sup> employed a metallic screen coated with a cellulose acetate film. One disadvantage was the penetration of moisture through the film, resulting in rusting of the screen. To obviate this difficulty, Moss suggested that the screen be coated first with a light-resistant phenol resin (e.g., diphenylol propane-ketone resin) and then with the cellulose ester.

The use of colored phenol-aldehyde solutions for coating electric-light bulbs has been proposed.<sup>118</sup> Azo dyes are among the substances used in preparing colored phenol resin varnishes.<sup>119</sup> One method of adding fillers and coloring material to such varnishes is to knead them with the phenol resin under pressure and at a temperature at which the resin is in a semi-liquid state. This mixture is then dissolved in appropriate solvents.<sup>120</sup>

Fusible phenol-formaldehyde resins have been included in inks.<sup>121</sup> An ink for printing on fruits contains a phenolic solution of spirit color, a phenol-formaldehyde resin, amyl acetate, ethyl alcohol and a color lake.<sup>122</sup>

One of the interesting applications of phenol resins is in photographic processes, e.g., photo-engraving. In a method employed by Doelker<sup>123</sup> a metal plate is coated with an alkali-soluble phenol resin (stage A) sensitized with ammonium dichromate. The light-sensitiveness is increased by incorporating proteins. The portions of the layer exposed to light become insoluble in alkalies and therefore remain on the plate when a solution of potassium hydroxide is applied. After removal of the alkali-soluble portions the surface under the image is etched with an acid. In similar methods, compounds capable of liberating halogens (e.g., iodoform) when exposed to light are employed as sensitizers.<sup>124</sup>

<sup>112</sup> E. S. Barralet, British P. 338,223, 1929; *Chem. Abs.*, 1931, 25, 2255.

<sup>113</sup> British P. 356,318, 1930, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 4207.

<sup>114</sup> G. A. Richter, W. B. Van Arsdel and R. B. Hill, U. S. P. 1,905,749, April 25, 1933, to Brown Co.; *Chem. Abs.*, 1933, 27, 3636.

<sup>115</sup> A. P. Pisarenko, *Izvest. Tzentr. Nauch.-Issledov. Inst. Kozh. Prom.*, 1932, 1, 18; *Brit. Chem. Abs.*, 1934, 415.

<sup>116</sup> F. E. DeVries, U. S. P. 1,778,185, Oct. 14, 1930, to Vulcan Proofing Co.; *Chem. Abs.*, 1930, 24, 5952.

<sup>117</sup> W. H. Moss, U. S. P. 1,860,687, May 31, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 3888. British P. 307,462, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs.*, 1930, 205.

<sup>118</sup> British P. 335,617, 1929, to N.-V. Philips' Gloeilampenfabr.; *Chem. Abs.*, 1931, 25, 1449.

<sup>119</sup> British P. 285,058, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs.*, 1929, 366. French P. 648,089, 1928 and its addn. 35,472, 1928; *Chem. Abs.*, 1929, 23, 2841; 1930, 24, 3914.

<sup>120</sup> R. Hessen, British P. 414,435, 1934, to A. Nowack A.-G.; *Chem. Abs.*, 1935, 29, 626. French P. 750,574, 1933; *Chem. Abs.*, 1934, 28, 351. See also A. E. Verbyla, U. S. P. 2,000,003, Apr. 30, 1935, to Standard Varnish Works.

<sup>121</sup> H. Kurz and K. Albert, British P. 371,527, 1932; *Chem. Abs.*, 1933, 27, 3627. French P. 711,613, 1931; *Chem. Abs.*, 1932, 26, 1810.

<sup>122</sup> M. Sinozaki, Japanese P. 93,651, 1931; *Chem. Abs.*, 1933, 27, 1529.

<sup>123</sup> E. Doelker, British P. 183,817, 1922; *J.S.C.I.*, 1924, 43, 78B. See also J. M. Eder, *Camera (Luzern)*, 1925, 3, 133; *Chem. Abs.*, 1925, 19, 2171. Cf. an analogous procedure for decorating glass in which a phenol resin is employed as a protective coating over which sensitized bitumen is placed. (French P. 756,045, 1933, to Soc. ind. de faonnages sur glaces; *Chem. Abs.*, 1934, 28, 3146.)

<sup>124</sup> M. C. Beebe and A. Murray, U. S. P. 1,587,271 and 1,587,274, June 1, 1926, to Wadsworth Watch Case Co.; *Brit. Chem. Abs.*, B, 1926, 778. Canadian P. 263,644 and 263,645, 1926; *Chem. Abs.*, 1926, 20, 3655. M. C. Beebe, A. Murray and H. V. Herlinger, U. S. P. 1,587,269, 1,587,270, 1,587,272 and 1,587,273, June 1, 1926, to Wadsworth Watch Case Co.; *Brit. Chem. Abs.*, B, 1926, 778. Canadian P. 263,642, 263,643, 263,646 and 263,647, 1926; *Chem. Abs.*, 1926, 20, 3655. See also Chapters 24 and 33.

## Chapter 22

### Uses of Phenol-Aldehyde Resins

#### II. Moldings

Phenol-formaldehyde curing resins were commercially introduced toward the end of the first decade of this century.<sup>1</sup> At that time, the molding industry had reached very substantial proportions. Hard rubber,<sup>2</sup> natural resins and asphaltic compounds were all being utilized. Celluloid had attained a great popularity and the consumption of shellac (largely in the phonograph-record industry) taxed the production. However, shellac was advancing in price and was open to criticism on account of its low water-resistance and relatively low melting point. Both are decided weaknesses in the field of electrical insulation. Further, the fire hazard which is inherent in celluloid was undesirable. Therefore, it was a natural step to try the phenol-formaldehyde condensation products in the established fields.

The commercial success of the phenolic resins has been largely due to the work of Baekeland. He found that the initial condensation product (Bakelite A),<sup>3</sup> when pressed in a hot mold, was transformed into an infusible, but still relatively brittle, Bakelite B. The article could then be removed, replacing the mold in use. When a number had accumulated, the moldings were placed in a "Bakelizer"<sup>4</sup> where they were submitted to heat and pressure to complete the conversion to Bakelite C.<sup>5</sup> As finally obtained the molded objects were infusible, unattacked by nonoxidizing acids and inert to alcohol, acetone, paraffins and esters.<sup>6</sup> Such a procedure eliminated the lengthy drying processes used by the previous workers and so enabled accurately formed objects to be turned out rapidly.<sup>7</sup> The discovery

<sup>1</sup> Some of the earlier applications of the phenol-formaldehyde condensation products are found in Chapter 18.

<sup>2</sup> Concerning the improbability of phenol resins replacing hard rubber, see *India Rubber World*, 1929, 79, 70.

<sup>3</sup> See Chapter 15 for a discussion of the preparation and properties of Bakelite A, B and C.

<sup>4</sup> This apparatus is simply a container in which phenol-formaldehyde resins can be heated under pressure in an atmosphere of carbon dioxide or other gas. (See Fig. 57). The tendency of the molding to become spongy due to the escape of formaldehyde and water is counteracted by the pressure. Bakelizers have been used experimentally but have found very few commercial applications.

<sup>5</sup> L. H. Baekeland, *Ind. Eng. Chem.*, 1909, 1, 149. Among the numerous reviews on Bakelite and its electrical and mechanical properties the following may be mentioned: Clement and Riviere, *Chimie et industrie*, 1922, 8, 38; *Chem. Abs.*, 1922, 16, 3404. A. Marcia, *Ann. chim. sci. ind.*, 1920, 35-6, 54; *Chem. Abs.*, 1921, 15, 1909. G. Matsumoto, *J. Chem. Ind. (Japan)*, 1915, 18, (207); *J.S.C.I.*, 1915, 34, 1104. *Neueste Erfind. u. Erfahr.*, 1920, 47, 14; *Chimie et industrie*, 1921, 5, 73. W. S. Flight, *Beama*, 1921, 9, 542; *Chem. Abs.*, 1922, 16, 796. K. Brandenburger, *Kunststoffe*, 1934, 24, 25; *Chem. Abs.*, 1934, 28, 2472. W. N. Nuttall, *J.S.C.I.*, 1928, 47, 1367. H. M. Richardson, *Chem. Met. Eng.*, 1932, 39, 597. H. Chase, *Elec. Mfg.*, 1932, 10 (4), 20; *Chem. Abs.*, 1933, 27, 377. J. Geller, *Brennstoff-Chem.*, 1933, 13, 130; *Chem. Abs.*, 1932, 26, 6163. For reviews of the patents and discussion of the Bakelite patents as examples of double patenting, see R. Eller, *Kunststoffe*, 1916, 6, 45; *Chem. Abs.*, 1916, 10, 1377. C. Coffignier, *Rev. chim. ind.*, 1917, 26, 201; *Chem. Abs.*, 1918, 12, 96. O. Kausch, *Kunststoffe*, 1914, 4, 263; *Chem. Abs.*, 1914, 8, 3244. J. Ephraim, *Kunststoffe*, 1922, 12, 2, 53. J. Scheiber and S. Hamburger, *ibid.*, 1922, 12, 42.

<sup>6</sup> Laminated phenolic-resin bubble caps have shown their ability to outlast iron in a solvent-recovery plant providing they did not come into contact with boiling furfural or cresol concentrates, strong alkalis or oxidizing acids. G. W. Clark, *Chem. Met. Eng.*, 1934, 41, 542. Vessels made from phenol-formaldehyde condensation products are said not to affect the flavor of foods. British P. 291,403, 1927, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 1228.

<sup>7</sup> The possibility of eczema due to handling phenol-formaldehyde condensation products has been raised by O. Sachs (*Wiener klin. Wochschr.*, 1921, 34, 356; *Chem. Abs.*, 1922, 16, 2925) and W. Meyer (*Farben-Chem.*, 1933, 4, 453; *Chem. Abs.*, 1934, 28, 1205. *Pharm. Ztg.*, 1934, 79, 1148; *Chem. Abs.*, 1935, 29, 519). However, according to F. Pabst (*Farben-Chem.*, 1934, 5, 127; *Chem. Abs.*, 1934, 28, 3604), the cases reported are due to the extraordinary sensitiveness of the victims to phenol and formaldehyde.

of a resin which would cure in a mold represented a very important advance for the plastics industry.

### INCORPORATION OF FILLERS

Molding powders are made by incorporating the filler in the following ways:\*

1.) The powdered resin is ground together with the hardening agent, lubricant<sup>9</sup> and dye. This may be done by passing the ingredients several times through a high-speed grinder or by using a ball mill.<sup>10</sup> A typical set of proportions is given in Table 28.

TABLE 28.—*Typical Proportions for a Phenol-Formaldehyde Molding Powder.*

Ingredient	Parts by Weight
Resin . . . . .	45 0
Hardening agent . . . . .	4 5
Lubricant . . . . .	1 0
Dye . . . . .	0 5
Filler (wood flour) . . . . .	49 0
	<hr/> 100 0

The filler is added and blending continued until an intimate, uniform mixture is obtained. The material is then sheeted on hot rolls. No definite procedure for sheeting can be given as the technic varies with each composition and the particular molding requirements. The size and speed of the rolls is likewise a factor and a change from one set to another with the same composition almost always necessitates a change in the procedure. The milling step in general is to heat the rolls to a surface temperature sufficient to flux the binder and to regulate the distance between them to the best thickness of sheet. Enough composition is then put into the nip of the rolls to form a complete sheet about the circumference of one roll. The material will adhere to both rolls at the start but will gradually accumulate on one. When the resin begins to flux, as indicated by a change in color of the material, it is scraped off. By repeating the operation a number of times, a uniform sheet is gradually built up and when the composition has the required flowing and curing properties as determined by an actual molding test, it is removed and allowed to cool. By maintaining a constant temperature and a definitely timed sequence of operations, consecutive sheets having practically the same properties may be obtained. The cooled sheets<sup>11</sup> are broken into fragments and granulated to form a molding powder. One disadvantage of this method of blending resin and filler is the fact that only a mechanical mixture is obtained and a more intimate union is possible by other means described below.

2.) The filler can be incorporated with the binder before the condensation of the latter has been carried to the point where the product is solid. That is, one makes use of what is called the liquid A stage.<sup>12</sup> If the initial condensation product is prepared without the use of a catalyst, more aldehyde and an acid

\* In Chapter 65, a fuller account of the preparation of molding powders is given.

<sup>9</sup> E. E. Novotny and C. J. Romieux (U. S. P. 1,557,318, Oct. 13, 1925; *Chem. Abs.*, 1926, 20, 97) proposed to use lanolin as a lubricant.

<sup>10</sup> R. Hessen, French P. 713,976, 1931, to A. Nowack A.-G.; *Chem. Abs.*, 1932, 26, 1811.

<sup>11</sup> F. A. Upper (U. S. P. 1,963,253, June 19, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 5200. See also Carborundum Co., British P. 411,846, 1932, to Bakelite, Ltd.; *Brit. Chem. Abs. B*, 1934, 718) incorporated abrasive fillers with phenol-formaldehyde resins in the above manner and cut grinding wheels from the resulting sheet.

<sup>12</sup> French P. 700,853, 1930, to Robert Bosch A.-G.; *Chem. Abs.*, 1931, 25, 3782. (Ebonite filler) German P. 402,707, 1921, to "Esgam" Erfindungs- & Studien-Gesellschaft allogener Materialien m.b.H.; *Kunststoffe*, 1925, 15, 123.

catalyst are included in the composition.<sup>13</sup> A liquid reactive resin has also been used as a wetting agent to facilitate the incorporation of additional solid binder.<sup>14</sup> Similarly, Novotny<sup>15</sup> heated abrasive grains in an oven and mixed them while still hot with 5 per cent of powdered resin. The mass was stirred while cooling, coating each granule. The coated material could be stored until needed. It was then wet with a liquid resin (0.2-5.0 per cent of the weight of abrasive) and enough powdered solid binder to bring the concentration of the latter up to 17 per cent was incorporated. The mass was sieved, formed in molds and heated in an oven to complete the reaction.

3.) Various organic solvents may be used to assist in the thorough mixing of the phenolic condensation product and filler. Alcohol,<sup>16</sup> Cellosolve,<sup>17</sup> furfuryl alcohol,<sup>18</sup> high-boiling hydrocarbons,<sup>19</sup> gasoline,<sup>20</sup> and hydrogenated phenols<sup>21</sup> have all

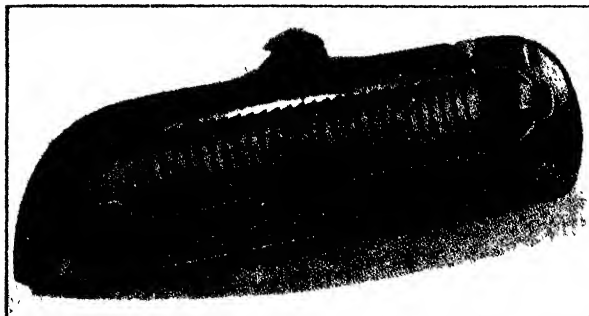


Fig. 74.  
An Asbestos - Braiding  
Shuttle Made of Bake-  
lite.

Courtesy Bakelite Corporation

been suggested. There are three ways in which the solvent may be employed: 1.) the filler may be wet with the liquid and dry binder added, 2.) the resin may be dissolved, the filler impregnated and the solvent evaporated or, 3.) part of the filler may be impregnated, dried and mixed with the rest. The last is stated by Loetscher<sup>22</sup> to be a cheap and satisfactory method of working. If the resin solution is heated until the condensation has reached the B stage, the resulting composition will mold faster<sup>23</sup> and be less tacky.<sup>24</sup> Tackiness can also be diminished by dissolving a dry brittle resin in the coating for the filler.<sup>25</sup>

4.) Some of the condensation products of phenols and formaldehyde retain part of their phenolic characteristics. Such bodies can be dissolved in aqueous alkali, mixed with a filler and then precipitated on it by acidification.<sup>26</sup> Peabody<sup>27</sup>

<sup>13</sup> G. Petrov, British P. 231,431, 1924; *Chem. Abs.*, 1925, 19, 3572. German P. 500,508, 1924, addn. to 380,596. *Chem. Abs.*, 1930, 24, 4906.

<sup>14</sup> N. P. Robie, British P. 333,409, 1928, to Carborundum Co., Ltd.; *Chem. Abs.*, 1931, 25, 573.

<sup>15</sup> E. E. Novotny, U. S. P. 1,901,325, Mar. 14, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3053.

<sup>16</sup> P. Colombi, French P. 646,879, 1928; *Chem. Abs.*, 1929, 23, 2258. See also F. A. Daniels and H. S. Snell, U. S. P. 1,732,398, Oct. 22, 1929, to Western Electric Co.; *Chem. Abs.*, 1930, 24, 213.

<sup>17</sup> C. A. Nash and R. S. Daniels, British P. 376,825, 1931, to Bakelite Corp., *Brit. Chem. Abs. B*, 1932, 949.

<sup>18</sup> E. E. Novotny and J. N. Kuzmick, U. S. P. 1,924,748, Aug. 29, 1933, to J. S. Stokes & Raybestos-Manhattan, Inc.; *Chem. Abs.*, 1933, 27, 5505.

<sup>19</sup> C. A. Nash, U. S. P. 1,343,575, June 15, 1920; *Chem. Abs.*, 1920, 14, 2401.

<sup>20</sup> A. Hawerlander, U. S. P. 1,877,864, Sept. 20, 1932, to Halizite Corp.; *Chem. Abs.*, 1933, 27, 382. British P. 336,754, 1929; *Chem. Abs.*, 1931, 25, 1966.

<sup>21</sup> E. Elbel and O. Sussenguth, U. S. P. 1,968,799, July 31, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 5951. British P. 369,571, 1930, *Brit. Chem. Abs. B*, 1933, 356.

<sup>22</sup> E. C. Loetscher, U. S. P. 1,959,375, May 22, 1934; *Chem. Abs.*, 1934, 28, 4564.

<sup>23</sup> E. Elbel and O. Sussenguth, U. S. P. 1,963,579, June 19, 1934, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 5284.

<sup>24</sup> British P. 359,986, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1932, 235.

<sup>25</sup> British P. 391,784, 1933, addn. to 359,986, 1930, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 4944.

<sup>26</sup> R. L. Seabury and L. W. Murray, U. S. P. 1,884,298, Oct. 25, 1932, to Delco-Remy Corp.; *Chem. Abs.*, 1933, 27, 918. Cf. the precipitation from alcoholic solution by the addition of water, C. A. Haanen, U. S. P. 1,630,424, May 31, 1927; *Chem. Abs.*, 1927, 21, 2385.

<sup>27</sup> J. C. Peabody, U. S. P. 1,083,755, Jan. 6, 1914; *Chem. Abs.*, 1914, 8, 871. Mention is made in



employed water as a wetting agent by adding the binder to paper pulp while on the beater. The paper on being formed into sheets carried the resin with it. Another procedure for incorporating a resin with paper pulp mixes a plastic condensation product with such fillers as slate dust, clay and pigments before kneading in wet fibrous material. Water is added finally to reduce the mass to a pulp.<sup>28</sup>

It has been stated that a thorough impregnation of the filler can be obtained by using emulsions.<sup>29</sup> Cheetham<sup>30</sup> drew resins directly from the reaction vessel into water containing gum arabic or other stabilizing agent. For example, 33 parts of the reactive phenol-aldehyde resinous material formed by refluxing 100 parts of phenol with 80 parts of 37.5 per cent formaldehyde solution and 0.5 part of sodium hydroxide for 30-90 minutes was mixed with 66-200 parts of water and 1-10 parts of gum arabic and passed through a colloid mill. The advantages which are stated to result from the use of aqueous emulsions are elimination of fire hazard, more rapid drying of the mass and more uniform distribution of the resin throughout the filler. According to Seebach,<sup>31</sup> the emulsions which he prepared by using a small amount of water (less than the amount of the resin) and less than the amount of alkali required to dissolve the resin could be broken by the addition of more water. In this way he precipitated the binder upon the filler.

5.) Furfural, benzaldehyde and other high-boiling aldehydes have been used as wetting agents. These substances act not only as solvents, but also as plasticizers and as supplementary hardening agents. Thus, Turkington<sup>32</sup> added 10 parts of furfural and about 8.3 parts of hexamethylenetetramine simultaneously to 100 parts of wood flour in a steam-heated kneading machine. To this mixture, 110 parts of a resin formed from 7.5 mols of phenol and 6 mols of formaldehyde were added slowly. The temperature throughout was held at about 100°C. The mass after cooling was ground and used as a molding powder. Other methods add furfural after partially mixing the dry resin and filler<sup>33</sup> or wet the binder with benzaldehyde before incorporating the diluent.<sup>34</sup>

Chapter 65 of several other proposals of the kind, i.e., those of Redman and Cheetham, Bakeland, Clapp, Wightman and Crossman. See also the application of xylenol condensation products to this process (E. E. Novotny, U. S. P. 1,771,138, July 22, 1930, to J. S. Stokes; *Chem. Abs.*, 1930, 24, 4564) and the preparation of this type of resin (Carleton Ellis, U. S. P. 1,980,987, Nov. 20, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1935, 29, 524).

<sup>28</sup> British P. 386,991, 1933, to Richardson Co.; *Chem. Abs.*, 1933, 27, 4674. See also British P. 383,636, 1931; *Brit. Chem. Abs. B.*, 1933, 102. Cf. R. H. Kienle and W. J. Schaeber, British P. 393,412, 1933, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 5910.

<sup>29</sup> Emulsions have been used to incorporate phenol-formaldehyde condensation products with, among others, abrasive fillers (K. Fickert, German P. 574,918, 1933; *Chem. Abs.*, 1933, 27, 4647) and felt (A. A. Mineev, *Izvestiya Tsentral. Nauch-Issledovatel. Inst. Kozhevnoi Prom.*, 1932, 6/7, 22; *Chem. Abs.*, 1934, 28, 6020).

<sup>30</sup> H. C. Cheetham, U. S. P. 1,976,433, Oct. 9, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 7563. See also U. S. P. 1,855,354, Apr. 26, 1932; *Chem. Abs.*, 1932, 26, 3344. French P. 659,015, 1930; *Chem. Abs.*, 1931 25, 1109. Cf. the stabilization of an emulsion of phenolic resin in toluene by the addition of a mixture of vinyl chloride and vinyl acetate. French P. 715,333, 1931, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 1994.

<sup>31</sup> F. Seebach, U. S. P. 1,720,062, July 9, 1929, to Bakelite G.m.b.H.; *Chem. Abs.*, 1929, 23, 4357. French P. 611,264, 1926; *Brit. Chem. Abs. B.*, 1927, 416. German P. 431,514, 1925; *Brit. Chem. Abs. B.*, 1926, 889. See also British P. 247,957, 1925; *Chem. Abs.*, 1927, 21, 860. British P. 384,728, 1931, to Bakelite Corp.; *Brit. Chem. Abs. B.*, 1933, 158.

<sup>32</sup> V. H. Turkington, U. S. P. 1,728,378, Sept. 17, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 5339. French P. 670,215, 1929; *Chem. Abs.*, 1930, 24, 1996. L. V. Redman and V. H. Turkington, U. S. P. 1,716,665, June 11, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 3822. British P. 330,968, 1929; *Chem. Abs.*, 1930, 24, 6042. French P. 676,469, 1929; *Chem. Abs.*, 1930, 24, 3092. German P. 519,792, 1924, to Bakelite G.m.b.H.; *Chem. Abs.*, 1931, 25, 3449. See also H. C. Martin, U. S. P. 1,937,043, Nov. 28, 1933, to Carborundum Co.; *Chem. Abs.*, 1934, 28, 1161. German P. 563,573, 1924, addn. to 541,374, 1924, to Bakelite G.m.b.H.; *Chem. Abs.*, 1933, 27, 1130. Cf. H. C. Martin, U. S. P. 1,576,440, Mar. 9, 1926; *Chem. Abs.*, 1926, 20, 1499. British P. 369,571, 1929, and 374,033, 1932, to Bakelite G.m.b.H.; *Chem. Abs.*, 1933, 27, 3096, 3795.

<sup>33</sup> F. P. Brock, U. S. P. 1,537,544, May 12, 1925, to Bakelite Corp.; *Chem. Abs.*, 1925, 19, 2116. German P. 541,374, 1924, to Bakelite G.m.b.H.; *Chem. Abs.*, 1932, 26, 2030.

<sup>34</sup> J. N. Kummick, U. S. P. 1,900,386, Mar. 7, 1933, to Manhattan Rubber Mfg. Div. of Raybestos-Manhattan, Inc., and J. S. Stokes; *Chem. Abs.*, 1933, 27, 3053.

6.) It has been stated that the amount of filler can be increased up to 95 per cent by incorporating it with the resin in the course of formation.<sup>35</sup> Nash<sup>36</sup> reports that a better control is had over the course of the reaction when the latter is carried out in the presence of solid diluents. Thus, a mixture of 50 parts of asbestos, 16.75 parts of cresol and 3.3 parts of hexamethylenetetramine was prepared. This composition was heated to not above 80°C. while stirring to ensure a uniform reaction. When the condensation had progressed to the desired extent, it was necessary only to discontinue heating to stop the reaction. Rolls of paper have been impregnated by passing first through an aqueous solution of hexamethylenetetramine, drying and then impregnating with a mixture of drying oil and phenol. The paper was heated finally to 100°C. or slightly above.<sup>37</sup>

**Inorganic Fillers.** Asbestos has been used extensively as a filler in moldings which must have considerable chemical resistance.<sup>38</sup> Aylsworth<sup>39</sup> stated that an asbestos-resin matrix withstood compression and did not have such a large coefficient of expansion as the phenol-formaldehyde condensation product itself. The material known as "Haveg" also contains asbestos and has proven useful in the manufacture of chemical apparatus.<sup>40</sup> The tensile strength is said to be about 2500 pounds per square inch; the transverse, 5500 pounds per square inch and the compressive, 10,500 pounds per square inch. This is sufficient to enable quite large vessels to be built, but in case greater mechanical strength is needed, metallic supports are employed (see Fig. 75).<sup>41</sup> Haveg is resistant to many chemicals, the principal exceptions being the strong oxidizing acids, hydrofluoric acid, bromine, iodine, caustic alkalies, acetone and aniline. A special grade is made which does not contain asbestos and is used where resistance to fluorides is required. Wirth has developed methods for coating the inner surfaces of pipes,<sup>42</sup> for covering solid surfaces (metal) with asbestos impregnated with phenol-formaldehyde resins,<sup>43</sup> for constructing large apparatus consisting of several sections,<sup>44</sup> and for building large apparatus reinforced with metal.<sup>45</sup> He has also prepared an acid-proof cement to be used in fastening together pieces of Haveg.<sup>46</sup> This cement was made by adding an acid to a liquid phenol-aldehyde condensation product shortly before use.

<sup>35</sup> R. Meyer, French P. 655,737, 1927; *Chem. Abs.*, 1929, 23, 4090.

<sup>36</sup> C. A. Nash, U. S. P. 1,692,856, Nov. 27, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1929, 23, 678. W. Hunter and J. G. Fairgrieve (U. S. P. 1,579,112, Mar. 30, 1926, to W. Tod, Jr., & Co., Ltd.; *Chem. Abs.*, 1926, 20, 1696. Canadian P. 245,651, 1924; *Chem. Abs.*, 1925, 19, 710. J. G. Fairgrieve, British P. 218,793, 1923, to Indurite Prod. Co., Ltd.; *Chem. Abs.*, 1925, 19, 581) state that oxycellulose containing calcium hypochlorite, which is obtained as a by-product in the manufacture of paper from esparto grass, is a good filler to use in this type of process. See also J. Mursch, U. S. P. 1,869,490, Aug. 2, 1932, to J. Gatti; *Chem. Abs.*, 1932, 26, 5440. (Waste paper used as a filler).

<sup>37</sup> A. L. Brown, U. S. P. 1,695,912, Dec. 18, 1928, to Westinghouse Electric & Mfg. Co.; *Chem. Abs.*, 1929, 23, 1002. See also British P. 298,793, 1927, to Stabilimenti Chimici Industriali; *Chem. Abs.*, 1929, 23, 8061.

<sup>38</sup> Brake bands and clutch facings have been made from asbestos fabric impregnated with phenol-formaldehyde resins.

<sup>39</sup> J. W. Aylsworth, U. S. P. 1,144,338, June 22, 1915, to Condensite Co.; *Chem. Abs.*, 1915, 9, 2296.

<sup>40</sup> According to J. K. Wirth (*Chem.-Ztg.*, 1925, 49, 653; *J.S.C.I.*, 1925, 44, 697B), Haveg consists of a Bakelite-type resin filled with an asbestos of high silica content. See also W. A. Adams, Jr., *Chem. Met. Eng.*, 1934, 41, 349. *Trans. Am. Inst. Chem. Eng.*, 1934, 30, 317. *Chem. Met. Eng.*, 1932, 39, 522; 1933, 40, 201. W. Peters, *Apparategbau*, 1926, 38, 195; *Chem. Abs.*, 1926, 20, 3363. A. I. Kogan and E. Yu. Kerman, *J. Chem. Ind. (Moscow)*, 1934, 4, 74; *Chem. Abs.*, 1934, 28, 4921. A similar material is called Faolite. See A. D. Sokolov and M. M. Bukhartzev, *Plast. Massui* 1934 (5) 7; *Chem. Abs.*, 1935, 29, 3069.

<sup>41</sup> A container weighing 1.8 tons has been constructed of a single piece of phenol-formaldehyde resin. No metallic supports were used. E. Kalman, *Chem. Fabr.*, 1929, 169; *Brit. Chem. Abs. B*, 1929, 529.

<sup>42</sup> T. F. von Haimberger and J. K. Wirth, U. S. P. 1,582,563, Apr. 27, 1926.

<sup>43</sup> J. K. Wirth, U. S. P. 1,582,566, Apr. 27, 1926; *Chem. Abs.*, 1926, 20, 2053.

<sup>44</sup> J. K. Wirth, U. S. P. 1,747,964, Feb. 18, 1930, and 1,789,642, Jan. 20, 1931; *Chem. Abs.*, 1930, 24, 1754; 1931, 25, 1401. British P. 265,566, 1926, to Säureschutz Ges.; *Chem. Abs.*, 1928, 22, 324.

<sup>45</sup> J. K. Wirth, U. S. P. 1,767,421, June 24, 1930; *Chem. Abs.*, 1930, 24, 4363. U. S. P. 1,949,135, Feb. 27, 1934; *Brit. Chem. Abs. B*, 1935, 321.

<sup>46</sup> J. K. Wirth, U. S. P. 1,867,960, July 19, 1932; *Chem. Abs.*, 1932, 26, 5183. British P. 292,334, 1927; *Brit. Chem. Abs. B*, 1928, 608.

Brake linings have been made from asbestos-filled phenol-aldehyde resins<sup>47</sup> and from mixtures of them with powdered iron,<sup>48</sup> lead<sup>49</sup> and vulcanized rubber.<sup>50</sup> A binder prepared by heating for 2-6 hours at 100-200°C. a mixture containing phenol (100 parts), formaldehyde (60-120 parts), oleic acid (20-60 parts) and ammonium oleate (1-15 parts) was proposed by Chapell.<sup>51</sup> With asbestos or powdered talc, mica or lead, it was to be used as a packing for steam pipes.

A mixture of asbestos and mica has been employed by Nash<sup>52</sup> in preparing a composition to be used for parts of fluid-meters. The filler constituted at least 60 per cent of the mixture and contained 5 per cent of mica. Mixed with asbestos, graphite, wood flour or powdered metals, mica has been used in making rubber-vulcanization molds.<sup>53</sup> One of the principal applications of mica has been in elec-

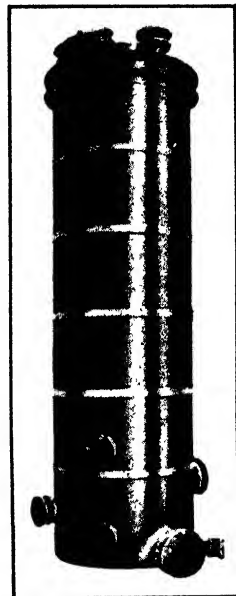


Fig. 75.

Tower Made of Haveg and Strengthened with Steel Bands.

*Courtesy Haveg Corp*

trical apparatus since it does not substantially increase the hysteresis-loss of the molded product.<sup>54</sup>

Although graphite has been employed as a filler in printing-matrices,<sup>55</sup> it has usually been added to molding compositions as a lubricant. In this way, a

<sup>47</sup> J. N. Longley, British P. 376,386, 1932, to Ferodo, Ltd.; *Chem. Abs.*, 1933, 27, 4044. See also I. J. Novak, U. S. P. 1,785,701, Dec. 16, 1930, to Raybestos-Manhattan, Inc.; *Chem. Abs.*, 1931, 25, 566.  
<sup>48</sup> German P. 543,071, 1926, to Kirchbach'sche Werke Kirchbach & Co.; *Chem. Abs.*, 1932, 26, 2561. British P. 272,478, 1927; *Brit. Chem. Abs. B*, 1923, 321.

<sup>49</sup> R. L. Seabury and L. W. Murray, U. S. P. 1,961,041, Aug. 7, 1934, to General Motors Corp.; *Chem. Abs.*, 1934, 28, 6259.

<sup>50</sup> A. T. K. Tseng, A. B. Kempel and R. Schar, U. S. P. 1,963,511, June 19, 1934, to Rex-Hide Rubber Mfg. Co.; *Chem. Abs.*, 1934, 28, 5192.

<sup>51</sup> M. L. Chapell, U. S. P. 1,102,473, July 7, 1914; *Chem. Abs.*, 1914, 8, 2926. See also L. H. Baekeland, U. S. P. 941,605, Nov. 30, 1909; *Chem. Abs.*, 1910, 4, 499.

<sup>52</sup> C. A. Nash, U. S. P. 1,942,874, Jan. 9, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 1830. British P. 346,349, 1929; *Chem. Abs.*, 1932, 26, 4191.

<sup>53</sup> G. W. Crosby, U. S. P. 1,920,139, July 25, 1933, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 4958. British P. 352,519 and 354,770, 1929; *Chem. Abs.*, 1933, 27, 450, 447.

<sup>54</sup> L. M. Hull, U. S. P. 1,705,576, Apr. 9, 1929, to Radio Frequency Labs.; *Chem. Abs.*, 1929, 23, 2585. French P. 688,149, 1930, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 754. F. Groff, U. S. P. 1,931,958, Oct. 24, 1933, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 663. French P. 698,183, 1930; *Chem. Abs.*, 1931, 25, 8185. (Uses rosin and a hexamethylene-triphenol type resin with the filler.)

<sup>55</sup> M. Smith, British P. 385,126, 1930, to Anglo Pencil Co., Ltd., and Pollopas, Ltd.; *Chem. Abs.*, 1933, 27, 2032.

number of self-lubricating bearings have been made.<sup>56</sup> Kempton<sup>57</sup> molded pulleys with a graphite-containing insert at the center whereas Volet<sup>58</sup> added graphite and a good electrical conductor (powdered copper) to phenol-formaldehyde resins to make brushes for motors.

Since the early days of the phenol-aldehyde resins there has been a great advance scored in the manufacture of abrasive articles. Improvement became imperative as grinding wheels in industry are being run at higher speeds, in order that increased rates of production may be established. Wheel bonds, therefore, must be made stronger, tougher and more uniform, in order to maintain a sufficient factor of safety. Phenol-formaldehyde-bonded wheels for rough grinding of steel castings (so-called "snagging") have been made which can be safely operated at a peripheral speed of 9000 feet per minute.<sup>59</sup> Both the vitrified- and shellac-bonded wheels have been largely displaced by those containing synthetic resins. Grinding wheels are employed in the automobile industry for numerous operations in many cases displacing circular saws. A number of abrasives have been suggested, carborundum, emery and corundum being the commonest.<sup>60</sup> A typical mixture contains 3-10 parts of abrasive grains and 1 part of phenolic binder, the latter being filled with 5-35 per cent of finely divided Cellite, fuller's earth or powdered quartz. By adjusting the pressure under which the mass is compacted varying degrees of porosity may be obtained.<sup>61</sup> Trivalent metal oxides, e.g., aluminum, chromium and ferric oxides, prepared by calcining the corresponding hydroxides, have been utilized in making polishing wheels from phenol-condensation products.<sup>62</sup> A further use of abrasive-filled phenol-aldehyde resins is the production of safety-treads.<sup>63</sup>

A number of inorganic fillers remain to be mentioned. Potassium chlorate (or perchlorate)<sup>64</sup> is employed to make heaters for blasting-cartridges. Phenol-formaldehyde resins have been used as binders in waterproof matches.<sup>65</sup> The addition of manganese dioxide (0.5-5.0 per cent) to molding compositions is said by Novotny<sup>66</sup> to improve flow and plasticity and to keep the molds in a clean and polished condition. Shields which are opaque to x-rays have been made using 75-95 per cent of barium sulphate.<sup>67</sup> Iron and steel fillers have been incorporated when magnetic properties were desired as in the construction of cores for induction coils<sup>68</sup> and diaphragms for telephones.<sup>69</sup> In the latter case, paper pulp was

<sup>56</sup> L. H. Baekeland, U. S. P. 1,054,265, Feb. 25, 1913; *Chem. Abs.*, 1913, 7, 1404. British P. 263,497, 1925, to Soc. anon. le Carbone. *Chem. Abs.*, 1928, 22, 145. British P. 285,078, 1927, Kirchbach'sche Werke Kirchbach & Co., *Chem. Abs.*, 1928, 22, 4741. Cf. British P. 275,648, 1926, Soc. anon. français du Ferodo; *Chem. Abs.*, 1928, 22, 2248. German P. 413,863, 1920, to Ferodo, Ltd.; *Kunststoffe*, 1925, 15, 165.

<sup>57</sup> W. H. Kempton, U. S. P. 1,392,173 and 1,392,174, Sept. 27, 1921; *Chem. Abs.*, 1922, 16, 320.

<sup>58</sup> R. A. L. Volet, British P. 270,271, 1928; *Chem. Abs.*, 1928, 22, 1447.

<sup>59</sup> L. H. Milligan, *Ind. Eng. Chem.*, 1927, 19, 1127. *Plastics*, 1928, 4, 346.

<sup>60</sup> L. H. Baekeland, U. S. P. 942,808, Dec. 7, 1909; *Chem. Abs.*, 1910, 4, 680. R. S. Daniels, British P. 353,019, 1929, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 382. French P. 692,733, 1930; *Chem. Abs.*, 1931, 25, 1651. P. Vogeli-Jaggi, British P. 406,921, 1934, to Diamantschleiferei Voegeli & Witz A.-G.; *Chem. Abs.*, 1934, 28, 5200.

<sup>61</sup> H. C. Martin, U. S. Reissue 17,740, July 22, 1930, to Carborundum Co.; *Chem. Abs.*, 1930, 24, 4605.

<sup>62</sup> German P. 593,499, 1934, to Deutsche Carborundum-Werke G.m.b.H.; *Chem. Abs.*, 1934, 28, 3199.

<sup>63</sup> G. Hopp, U. S. P. 1,156,081, Oct. 12, 1915; *Chem. Abs.*, 1915, 9, 3333.

<sup>64</sup> A. C. Scott, British P. 391,881, 1933; *Chem. Abs.*, 1933, 27, 5541. French P. 745,098, 1933, to Heaters, Ltd.; *Chem. Abs.*, 1933, 27, 4402.

<sup>65</sup> L. E. Larsson, British P. 414,938, 1933; *Brit. Chem. Abs. B*, 1934, 942. See also H. W. Robinson, British P. 265,378, 1926; *Brit. Chem. Abs. B*, 1927, 269. Cf. British P. 298,948, 1927, to Soc. Italiane Polveri Esplodenti; *Chem. Abs.*, 1929, 23, 3102.

<sup>66</sup> E. E. Novotny, U. S. P. 1,964,423, Dec. 18, 1934, to J. S. Stokes; *Chem. Abs.*, 1935, 29, 855.

<sup>67</sup> P. E. Harth, British P. 280,636, 1926; *Chem. Abs.*, 1928, 22, 3070.

<sup>68</sup> E. Kramer, U. S. P. 1,832,937, Nov. 24, 1931, to Hartstoff-Metall A.-G.; *Chem. Abs.*, 1932, 26, 1079. British P. 348,338, 1929; *Chem. Abs.*, 1932, 26, 3887. P. N. Rosebv, U. S. P. 1,790,477, Jan. 20, 1931, to Associated Telephone & Telegraph Co.; *Chem. Abs.*, 1931, 25, 1348. P. N. Rosebv, U. S. P. 1,850,181, Mar. 22, 1932, to Automatic Telephone Mfg. Co., Ltd.; *Chem. Abs.*, 1932, 26, 2834. British P. 318,953, 1928, 328,974, 342,999, 343,020, 1929; *Chem. Abs.*, 1930, 24, 2562, 5446; 1932, 26, 3887. Cf. British P. 308,315, 1923, to International General Elec. Co.; *Chem. Abs.*, 1930, 24, 177. W. J. Polydoroff, British P. 403,368, 1933, to Johnson Laboratories, Inc.; *Chem. Abs.*, 1934, 28, 3198.

<sup>69</sup> J. M. Taylor, U. S. P. 1,514,406, Nov. 4, 1924, to Diamond State Fibre Co.; *Chem. Abs.*, 1925, 19, 157.

included as an additional filler. Noftzger<sup>70</sup> reports that bearings can be produced from 60-80 per cent of a schist which is found at Buckeye, Ariz., held together with a phenol-aldehyde binder. Pencils have been made using talc as a lubricant and eosin as the coloring agent.<sup>71</sup> Electrical insulation has been prepared by driving off a phenolic binder at 1100°C. from a talc-filled composition.<sup>72</sup> Further, charcoal and coke,<sup>73</sup> powdered stone,<sup>74</sup> cement,<sup>75</sup> slag<sup>76</sup> and calcined magnesia with a solution of zinc sulphate<sup>77</sup> have all been suggested as ingredients in plastic masses of the phenol type.

**Organic Fillers.** The commonest organic filler is wood flour.<sup>78</sup> Pieces pressed from wood-flour-filled phenolic resins can be made very accurately. The articles come from well-made molds with a high polish, have a higher dielectric strength than those made using asbestos and can be used at temperatures up to 120°C. Insulating pieces made from wood flour and phenol-aldehyde resins have been extensively used on automobile lighting and ignition systems, for lamp sockets, telephone parts and oil-immersed transformer insulators. Syono<sup>79</sup> states that articles which contain new wood cellulose retain a lacquer firmly. The addition of 0.5 part of pine tar to a mixture of 4 parts of phenolic resin, 3 parts of wood flour and 6 parts of powdered charcoal is said by Omansky<sup>80</sup> to produce a composition which flows easily in the mold and so gives accurate moldings.

Short cordage fibers, e.g., hemp and sisal, have also been suggested as fillers.<sup>81</sup> For example, a mixture of phenol-formaldehyde resol (700 parts), chopped manila hemp (600 parts), hexamethylenetetramine (227 parts of a 35.7 per cent alcoholic solution), methylated spirit (53 parts), aluminum stearate (24 parts) and nigrosine (28 parts) was dried at 60°C., ground and molded at 340°C. for 4 min. at 2000 pounds per square inch pressure. Herper<sup>82</sup> reports that exposing chips of wood or sawdust to a steam pressure of 58 kg. per sq. cm. for 4-5 sec. and suddenly releasing the pressure disintegrates the cellulosic material into fibers which can then be bound together with a phenol-formaldehyde resin. The product is light and has a tensile strength of 280-365 kg. per sq. cm.<sup>83</sup> A more thorough impregnation of fiber is obtained, according to Mellanoff,<sup>84</sup> if a condensation product of phenol, an alkaline extract of peat and formaldehyde is used as the binder.

The interspersing of a binder among long fibers is difficult by the methods previously mentioned. This is because the fibrous material mats together and

<sup>70</sup> C. F. Noftzger, U. S. P. 1,791,834, Feb. 10, 1931; *Chem. Abs.*, 1931, 25, 1957

<sup>71</sup> E. Rademacher, British P. 391,798, 1933; *Chem. Abs.*, 1933, 27, 5494. See also H. Mayer, German P. 535,981, 1927, to Deka-Textulfarben A.-G.; *Chem. Abs.*, 1932, 26, 1134

<sup>72</sup> T. C. Prouty, U. S. P. 1,453,726, May 1, 1923; *Chem. Abs.*, 1923, 17, 2335

<sup>73</sup> German P. 555,657, 1933, to Presswerk Königstein G. m. b. H.; *Chem. Abs.*, 1934, 28, 1560.

<sup>74</sup> P. Meyer, Canadian P. 272,199, 1927; *Chem. Abs.*, 1927, 21, 3726.

<sup>75</sup> A. Krieger, German P. 508,659, 1927; *Chem. Abs.*, 1931, 25, 791.

<sup>76</sup> S. F. Walton, U. S. P. 1,781,204, Nov. 11, 1930, to Exolon Co.; *Chem. Abs.*, 1931, 25, 177.

<sup>77</sup> G. Bia and J. E. D. de Granville de Bielze, British P. 275,448, 1926; *Chem. Abs.*, 1928, 22, 2254.

<sup>78</sup> British P. 334,804, 1928, to Bois Bakelite and La Bakelite; *Chem. Abs.*, 1931, 25, 140. French P. 665,398, 1928; *Chem. Abs.*, 1930, 24, 930. British P. 276,440, 1926, to Products Protection Corp.; *Chem. Abs.*, 1928, 22, 2445. H. Swan and S. Higgins, U. S. P. 1,973,348, Sept. 11, 1934; *Chem. Abs.*, 1934, 28, 6958. Pulverized birch wood is suggested by J. R. Köhler, Swedish P. 65,096, 1928; *Chem. Abs.*, 1930, 24, 1476.

<sup>79</sup> T. Syono, Japanese P. 90,944, 1931; *Chem. Abs.*, 1932, 26, 1460.

<sup>80</sup> M. Omansky, U. S. P. 1,969,146, Aug. 7, 1934, to E. W. Colledge, General Sales Agent, Inc.; *Chem. Abs.*, 1934, 28, 6257.

<sup>81</sup> R. Greenhalgh, British P. 377,979, 1932, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 4042. See also H. Kline, British P. 347,788, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B.*, 1931, 729. M. M. Allen (*British Plastics*, 1934, 6, 208; *Chem. Abs.*, 1935, 29, 3068) states that cracks, caused by uneven shrinkage or expansion, can be avoided by using fabric fillers instead of wood flour.

<sup>82</sup> H. Herper, *Kunststoffe*, 1928, 18, 127; *Chem. Abs.*, 1928, 22, 3268.

<sup>83</sup> Wood fibers containing a large percentage of α-cellulose are mentioned by G. E. Wightman, British P. 345,332, 1928, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 435. See also British P. 338,120, 1929; *Chem. Abs.*, 1933, 26, 4458. French P. 686,772, 1929; *Chem. Abs.*, 1931, 25, 835.

<sup>84</sup> I. S. Mellanoff, U. S. P. 1,857,690, May 10, 1932, to Kemikal, Inc.; *Chem. Abs.*, 1932, 26, 3885. Cf. R. Armenault and J. Malet, French P. 679,342, 1928, to Fabriques de prod. de chim. org. de Laire (S. a.); *Chem. Abs.*, 1930, 24, 3867.

prevents uniform admixture of dry resin, and in the wet method of operation a lumpy product is obtained which must be ground, with resultant destruction of the fiber length. Kempton<sup>88</sup> stated that this difficulty could be overcome by impregnation of cloth, which after drying was chopped, shredded or ground to a loose fluffy mass of long fibers. Chamberlin<sup>89</sup> suggested that the impregnated fabric be cut into pieces and not shredded. In this way impact molding material<sup>90</sup> is made and bridges the gap between the usual molding compositions and the laminated (see Fig. 76). Like the former it is shaped in a mold and does not require machining, whereas like the latter it possesses a high impact strength (30 foot-pounds per inch square is possible as compared to 3.5 for wood-flour-filled). The strongest impact material requires about 5000 pounds per square inch to shape it but, nevertheless, it has found use in the manufacture of gears,<sup>91</sup> handles for tools, pump rotors and other articles which require considerable resistance to shock.<sup>92</sup>

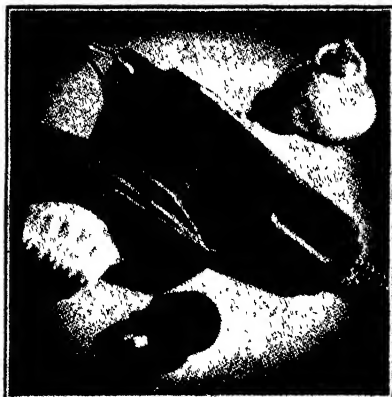


FIG. 76.  
Bakelite Impact-Resisting Housing for an  
Electric Vibrator.

*Courtesy Bakelite Corporation*

When the usual organic fillers are employed, a considerable amount of resin is used in saturating the fibers. According to Hurst,<sup>93</sup> this assumed loss of binding material can be diminished by using cottonseed hulls. Thus, a mixture of 78 parts of cottonseed hulls, 20 parts of phenolic resin and 2 parts of dye molded satisfactorily at a pressure of 800 pounds per square inch and a temperature of 150°C.

A number of other organic fillers have been suggested. Ground phenol-resin

<sup>88</sup> W. H. Kempton, U. S. P. 1,513,323, Oct. 28, 1924, to Westinghouse Electric & Mfg. Co.; *Chem. Abs.*, 1925, 19, 156. General Elec. Co., British P. 193,910, 1922, to Brit. Thomson-Houston Co., Ltd.; *J.S.C.I.*, 1923, 42, 728A. See also R. Schroeder, British P. 278,038, 1926, to Jaroslaw's erste Glimmerware-Fabr.; *Brit. Chem. Abs. B*, 1928, 48. Cf. the use of threads or cords as a filler, British P. 353,070, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 936. *Chem. Met. Eng.*, 1932, 39, 522.

<sup>89</sup> C. L. Chamberlin, British P. 316,275, 1928, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1930, 157. Molded objects have been reinforced with canvas by J. A. Crabtree and J. R. Dolphin, British P. 322,434, 1928; *Chem. Abs.*, 1930, 24, 2816.

<sup>90</sup> The name "impact molding material" refers to the fact that articles molded from such compositions are especially resistant to impact.

<sup>91</sup> *Plastics*, 1928, 2, 155. See also L. T. Frederick, U. S. P. 1,831,063, Nov. 10, 1931, to Continental Diamond Fibre Co.; *Chem. Abs.*, 1932, 26, 815. H. L. Johnston (U. S. P. 1,482,847, Feb. 5, 1924, to Hobart Mfg. Co.; *Chem. Abs.*, 1924, 18, 1037) has used small pieces of sponge in molding silent gears.

<sup>92</sup> Cf. the preparation of hammers from impact material and from laminated stock. Allgem. Elektrizitäts-Ges., British P. 311,418, 1928, to International General Elec. Co.; *Chem. Abs.*, 1930, 24, 930.

<sup>93</sup> I. A. Hurst, U. S. P. 1,893,540, June 14, 1932, to General Elec. Co.; *Chem. Abs.*, 1932, 26, 4192. German P. 598,193, 1934, to Allgem. Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 5604. British P. 386,782, 1933, to Brit. Thomson-Houston Co.; *Chem. Abs.*, 1933, 27, 5996.

scrap is stated to give a uniform molding.<sup>91</sup> Ebonite,<sup>92</sup> sulphite waste,<sup>93</sup> ground cork,<sup>94</sup> hydrocellulose,<sup>95</sup> cellulose acetate<sup>96</sup> and cellulosic materials which had previously been treated with an oxidizing agent<sup>97</sup> have all been mentioned. Vegetable ivory bound with the product of permanganate oxidation of a phenol-formaldehyde resin has been used as a heat-insulating material for handles of cooking vessels.<sup>98</sup> Bormans<sup>99</sup> molded billiard balls from a phenolic resin filled with ivory scrap. The incorporation of soap as a lubricant in phonograph records of the phenol type has been suggested by Whyte.<sup>100</sup>

### MOLDING OF PHENOLIC RESINS

The molds<sup>101</sup> employed must withstand working pressures of over 1000 pounds per square inch and, in order to permit the temperature to be increased and decreased as rapidly as possible, they must contain a minimum of metal. The result is that the molds are usually made of a good grade of hardened steel. If the finished article is to have a smooth surface, the mold is highly polished, chromium plating being occasionally employed. Further, the molds have to be designed with sufficient head capacity to accommodate the molding composition which often occupies 3-4 times the volume of the finished piece. Hydraulic presses are employed which have capacities ranging from 5 tons upward and platens heated by steam, gas or electricity. The molds are heated either directly or by conduction from the platens.

The charge of powder is placed in the mold while the latter is at a temperature of about 90°C. The filled mold is placed immediately in the press, the platens of which are at 150-250°C. depending on the mixture used.<sup>102</sup> The press is closed and a pressure of 2000-3000 pounds per square inch is applied. The time required before the molded article may be removed depends on the molding powder and on the size and shape of the object. This period has been steadily decreased and for small pieces 0.5-1.0 minute is approximately the present requirement, whereas larger bodies may take 5-10 minutes. At one time, the moldings were finally baked in an oven to complete the condensation, remove any water formed in the reaction and to increase the dielectric strength.<sup>103</sup> Another former custom was to refrain from removing the article until the temperature

<sup>91</sup> J. W. Aylsworth, U. S. P. 1,102,631, July 7, 1914, to Condensite Co. of Amer.; *Chem. Abs.*, 1914, 8, 3127. See also H. Mens, British P. 335,219, 1929, addn. to 335,194, 1929, to Chemie & Technik J. M. S., G.m.b.H.; *Brit. Chem. Abs. B*, 1930, 1120. E. Noack (British P. 290,801, 1927; *Chem. Abs.*, 1929, 23, 943) employed powdered phenolic resin as a filler for asphalt.

<sup>92</sup> F. J. Crosley, British P. 355,341, 1930, to India-Rubber Gutta-Percha & Telegraph Works Co., Ltd.; *Brit. Chem. Abs. B*, 1931, 984. See also J. Poberejsky, French P. 656,760, 1927; *Chem. Abs.*, 1929, 23, 4307.

<sup>93</sup> F. J. Wallace, British P. 370,752, 1931, to Robeson Process Co.; *Brit. Chem. Abs. B*, 1932, 614. French P. 719,894, 1931; *Chem. Abs.*, 1932, 26, 3945.

<sup>94</sup> French P. 771,759, 1934, to Bond Mfg. Co.; *Chem. Abs.*, 1935, 29, 1541.

<sup>95</sup> G. S. Petrov, Russian P. 360, 1920; *Chem. Abs.*, 1933, 27, 4562.

<sup>96</sup> A. J. Weith and O. Holzman, U. S. P. 1,720,192, July 9, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 4357. British P. 326,840, 1928; *Brit. Chem. Abs. B*, 1930, 624. French P. 670,761, 1929; *Chem. Abs.*, 1930, 24, 1996. See also M. Melamid, French P. 677,854, 1929; *Chem. Abs.*, 1930, 24, 3332.

<sup>97</sup> British P. 322,158, 1928, and 331,851, 1929, to Magnasco, Roggero & Co.; *Brit. Chem. Abs. B*, 1930, 111, 872.

<sup>98</sup> C. Schmidt, British P. 326,255, 1928; *Brit. Chem. Abs. B*, 1930, 469. German P. 461,009, 1926; *Brit. Chem. Abs. B*, 1930, 469. Vegetable ivory together with magnesium cement has been employed as a filler for artificial stone. British P. 301,893, 1928, to E. Teltschik & Co.; *Brit. Chem. Abs. B*, 1929, 853.

<sup>99</sup> E. Bormans, British P. 369,252, 1930; *Chem. Abs.*, 1933, 27, 2321. French P. 711,629, 1930; *Chem. Abs.*, 1932, 26, 3025.

<sup>100</sup> S. Whyte, British P. 362,445, 1930, to Gramophone Co., Ltd.; *Chem. Abs.*, 1933, 27, 1117.

<sup>101</sup> See Chapters 67 and 68 for descriptions of molding equipment and general methods of molding.

<sup>102</sup> Wall tiles having one surface polished and the other porous have been obtained by heating one press platen to a higher temperature than the other, A. V. Keller, British P. 344,276, 1930; *Chem. Abs.*, 1932, 26, 3880.

<sup>103</sup> G. L. Peakes (U. S. P. 1,602,249, Oct. 5, 1926, to Bakelite Corp.; *Chem. Abs.*, 1926, 20, 3796. British P. 275,011, 1926; *Brit. Chem. Abs. B*, 1927, 756) mentions heating at 125-135°C. for 70-80 hours, increasing the dielectric strength in some cases 70-80 per cent.

had been reduced to 95°C. Both of these practices have to a great extent been eliminated by the use of improved molding powders.

Some investigators have employed condensation products which were no longer truly fusible, but which softened enough at an elevated temperature to enable molding to take place. Aylsworth prepared phonograph records<sup>104</sup> and printing plates<sup>105</sup> from blanks which had previously been baked until almost complete hardening had taken place. Such blanks could be removed more rapidly from the expensive record mold than could those made using fusible compositions. It has been further stated that adhesion to the mold and blemishes due to the evolution of gases do not appear when relatively infusible condensation products are used.<sup>106</sup> Die pressing has been employed as a means of making troughs from sheets of phenolic resin in the C stage.<sup>107</sup>

Hollow balls containing compressed air have been made by Aylsworth and Smith<sup>108</sup> through welding together two hemispherical shells of partially reacted resin. The top half of the ball was placed in the plunger of a press which, as it moved downward, drove the enclosed air into the center. Hollow cylinders have been produced by using rotating molds, centrifugal force holding the contents in place during hardening.<sup>109</sup> Novotny<sup>110</sup> inserted pieces of solid carbon dioxide within the mass of material to be molded. As the temperature was raised, the solid volatilized, driving the plastic composition to the walls of the mold and forming a hollow object. Since very reactive resins can be controlled at the temperature of "dry ice" the addition of the latter was stated to enable the molding time to be cut down.<sup>111</sup> Stream-line tail pieces for airplane motor-generator sets have been formed by compacting paper pulp around a core, drying and impregnating with phenolic condensation products. The latter were finally cured under heat and pressure.<sup>112</sup>

The molding of dental plates differs from that of most articles in that a large number of identical objects is not required. Therefore, methods have been devised for using plaster of Paris molds which can be economically prepared. For example, porcelain teeth<sup>113</sup> are inserted in a denture made of wax. This is then surrounded with plaster of Paris and the wax is melted out leaving the teeth *in situ*.<sup>114</sup> The mold is painted with linseed oil to keep the molding from sticking to the plaster and the phenolic resin is added in the plastic state. The two halves of the mold are clamped together and heated in an autoclave (containing methylated spirits) to 121-149°C.<sup>115</sup> The finished article can be filed, sandpapered

<sup>104</sup> J. W. Aylsworth, U. S. P. 1,146,388, July 13, 1915; *Chem. Abs.*, 1915, 9, 2432. Cf. T. A. Edison, U. S. P. 1,411,425, Apr. 4, 1922, to New Jersey Patent Co.; *Chem. Abs.*, 1922, 16, 2014.

<sup>105</sup> J. W. Aylsworth, U. S. P. 1,098,610, June 2, 1914, to Condensite Co. of Amer.; *Chem. Abs.*, 1914, 8, 2782.

<sup>106</sup> Cf. E. E. Novotny, U. S. P. 1,398,149, Nov. 22, 1921, and 1,451,783, Apr. 17, 1923, to J. S. Stokes; *Chem. Abs.*, 1922, 16, 802.

<sup>107</sup> British P. 371,344, Apr. 18, 1932, to "Herold" A.-G.; *Chem. Abs.*, 1933, 27, 3629.

<sup>108</sup> J. W. Aylsworth and D. Smith, U. S. P. 1,134,433, Apr. 6, 1915, to Condensite Co. of Amer.

<sup>109</sup> F. Pollak, British P. 14,490, 1915; *J.S.C.I.*, 1916, 35, 1226. See also N. E. Duffy, British P. 136,862, to Vickers, Ltd.; *Kunststoffe*, 1925, 15, 44. Similar rotating molds have been used in the fashioning of both cylindrical and disc phonograph records. J. W. Aylsworth, U. S. P. 1,146,384, 1,146,385 and 1,146,389, July 13, 1915, to Condensite Co. of Amer.; *Chem. Abs.*, 1915, 9, 2432.

<sup>110</sup> E. E. Novotny, U. S. P. 1,776,366, Sept. 23, 1930, to J. S. Stokes; *Chem. Abs.*, 1930, 24, 5518.

<sup>111</sup> E. E. Novotny (U. S. P. 1,901,324, Mar. 14, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3053) has also used solid carbon dioxide to keep abrasive grains coated with a sticky resin temporarily free-flowing.

<sup>112</sup> L. T. Frederick, U. S. P. 1,475,764, Nov. 27, 1923; *Chem. Abs.*, 1924, 18, 574.

<sup>113</sup> Teeth have been made from phenol-aldehyde resins. Pure tin was used for the mold. A. F. van Renterghem, German P. 508,820, 1928; *Chem. Abs.*, 1931, 25, 787.

<sup>114</sup> C. H. Wardell (U. S. P. 1,742,430, Jan. 7, 1930, to Ohio Chemical & Mfg. Co.; *Chem. Abs.*, 1930, 24, 1189. British P. 275,541, 1926; *Chem. Abs.*, 1928, 22, 2254) suggests coating the teeth with a yielding material to prevent breakage. See also H. J. Grange and S. W. Wilding, U. S. P. 1,669,557, May 15, 1928; *Chem. Abs.*, 1928, 22, 2446. British P. 258,674, 1925, to Amalgamated Dental Co., Ltd.; *Chem. Abs.*, 1927, 21, 3109.

<sup>115</sup> E. Wieland (U. S. P. 1,639,475, Aug. 16, 1927; *Chem. Abs.*, 1927, 21, 3276) suggested that the temperature be raised slowly to not above 80°C.



and polished.<sup>116</sup> It was also suggested that a similar procedure could be used to face ebonite dentures with a phenol-aldehyde resin.<sup>117</sup> Noyes<sup>118</sup> reinforced dental plates molded from phenolic resins with strips of fabric.

Since the mold in which a denture is formed need not be used again, Mombach<sup>119</sup> recommended that a metal powder be added to the plaster. When the molding was to be removed, the investment could be treated with acid, liberating hydrogen and decomposing the mold. In this way, the shaped structure could be freed. Lebach and Wirth<sup>120</sup> state that articles can be readily separated from metal molds providing the latter are first coated with a celluloid lacquer. If flat objects are being formed, newsprint impregnated with sodium bisulphate can be used. The celluloid and the impregnated paper are both destroyed at the temperature at which the resin is plastic.

In case the condensation of the phenol and the aldehyde is allowed to go too far, the product may still be partially thermoplastic, but not enough to give a good molding. Weber<sup>121</sup> has described such a resin which was made by refluxing 100 parts of phenol, 100 parts of formaldehyde (40 per cent solution) and 12.5 parts of concentrated ammonia until the product was a rubbery semi-solid mass. The aqueous solution was separated from the resulting resin, the latter was allowed to cool and was then crushed to a fine powder. On molding at 160°C., the full 1000 pounds pressure could be applied within 30 seconds of closing the mold. At the end of 5 minutes' time the article was removed and found to be opaque and to have only a fair surface. Weber found, however, that the addition of hexamethylenetetramine-triphenol in the ratio of 2 parts to 10 caused the overcured resin to flow easily in the mold, giving a translucent article with a good surface. The hexamethylenetetramine-triphenol was prepared by refluxing 48 parts of hexamethylenetetramine with 94 parts of phenol in a solvent composed of 60 parts of ethyl alcohol and 40 parts of water. On cooling the solution, the compound crystallized out. A second crop of crystals was obtained by concentrating the mother liquor. The product could be purified by recrystallization from hot alcohol. The use of chlorinated naphthalene and chlorinated phenols as solid solvents assisting in the molding of phenolic resins was early suggested by Aylsworth;<sup>122</sup> and benzyl alcohol,<sup>123</sup> naphthalene, anthracene and cumarone resin<sup>124</sup> have also been proposed.

A loud-speaker diaphragm has been made by hot pressing at about 800 kg per sq. cm. a mixture of solid polymer of formaldehyde and powdered phenol.<sup>125</sup> Burmeister<sup>126</sup> reports that, using resorcinol in this operation, 2-5 minutes at 120-125°C. is sufficient time for most articles.

A number of investigators have suggested that metal reinforcements be included within the phenol-aldehyde molding to increase its strength. Thus, Layman<sup>127</sup> made handles for various articles by shaping the resin about a wire which carried at each end devices for attaching to the body. Wires have also been

<sup>116</sup> G. M. Hick and N. G. Hick, U. S. P. 1,585,348, May 18, 1926; *Chem. Abs.*, 1926, 20, 2233. British P. 249,223, 1924 and 269,037, 1926; *Chem. Abs.*, 1927, 21, 996; 1928, 22, 1447. See also F. Rasching chem. Fabr., British P. 353,870, 1930, to F. Rasching G.m.b.H.; *Brit. Chem. Abs.* B, 1931, 895. L. Oberlaender, British P. 238,446, 1924; *Chem. Abs.*, 1926, 20, 2053.

<sup>117</sup> See also M. L. Axelrod, British P. 262,410, 1925; *Chem. Abs.*, 1927, 21, 3719. Cf. S. W. Wilding, British P. 260,319, 1925, to Amalgamated Dental Co., Ltd.; *Chem. Abs.*, 1927, 21, 3432.

<sup>118</sup> S. E. Noyes, U. S. P. 1,784,250, Dec. 9, 1930, to Harrison-Noves Chem. Corp., Ltd.

<sup>119</sup> G. Mombach, U. S. P. 1,724,501, Aug. 13, 1929; *Chem. Abs.*, 1929, 23, 4784. See also M. L. Axelrod, British P. 260,287, 1925; *Chem. Abs.*, 1927, 21, 3432.

<sup>120</sup> H. Lebach and J. K. Wirth, U. S. P. 1,917,451, July 11, 1933, to Säureschutz G.m.b.H.; *Chem. Abs.*, 1933, 27, 4701.

<sup>121</sup> H. M. Weber, U. S. P. 1,720,406, July 9, 1929, to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 4357.

<sup>122</sup> J. W. Aylsworth, U. S. P. 1,046,137, Dec. 3, 1912, and 1,087,422, Feb. 17, 1914; *Chem. Abs.*, 1913, 7, 712; 1914, 8, 1354. U. S. Reissues 1,530 and 1,531, Oct. 8, 1918; *Chem. Abs.*, 1919, 13, 80. British P. 9,559, 1911; *Chem. Abs.*, 1912, 6, 2855. See also the use of pine tar mentioned above in connection with wood flour as a filler.

<sup>123</sup> A. Dormoy and G. Tanqueray, British P. 361,879, 1930; *Chem. Abs.*, 1933, 27, 1117.

<sup>124</sup> L. H. Baekeland, U. S. P. 1,259,472, Mar. 19, 1918; *Chem. Abs.*, 1918, 12, 1502.

<sup>125</sup> British P. 406,327, 1934, to Lohusta Elektro-Akustik G.m.b.H.; *Chem. Abs.*, 1934, 28, 4852.

<sup>126</sup> H. Burmeister, British P. 275,673, 1926; *Chem. Abs.*, 1928, 22, 2445. German P. 480,832, 1924; *Chem. Abs.*, 1929, 23, 5018.

<sup>127</sup> F. E. Layman, U. S. P. 1,625,322, Apr. 19, 1927, to Cutler-Hammer Mfg. Co.

used to reinforce abrasive wheels.<sup>128</sup> Moldings which were to be screwed on objects have been strengthened by metal inserts<sup>129</sup> at the point of attachment.<sup>130</sup> Kasch<sup>131</sup> stated that less material was required and that a more thorough and uniform fusion of the resin was obtained, if knobs and balls were molded around a hollow metal center. Laminated gears,<sup>132</sup> phonograph records<sup>133</sup> and panels<sup>134</sup> all have been strengthened with sheets of metal or wire gauze. Frederick<sup>135</sup> made a light telephone diaphragm by inserting a thin sheet of steel between layers of synthetic resin.

Numerous types of electrical apparatus have been molded from phenol resins, including distributor caps, spark coils,<sup>136</sup> commutators<sup>137</sup> and containers for primary batteries.<sup>138</sup> Groff<sup>139</sup> suggested that the metal parts of such apparatus be coated

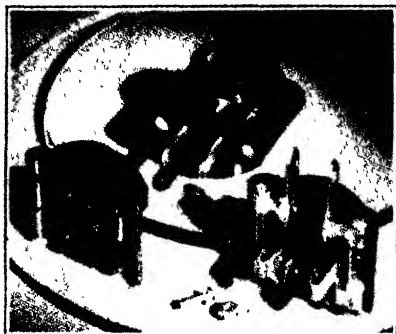


FIG. 77.—Bakelite Attachment Plug with Cartridge Fuses.

Courtesy Bakelite Corporation

with a layer of oil-modified phenolic resin<sup>140</sup> before placing in the mold. The bulk of the article was formed of an unmodified condensation product. This procedure was stated to result in a better insulation.<sup>141</sup>

Rubber inserts have been utilized as tires for castor wheels<sup>142</sup> and as protecting rings around electrical attachment plugs.<sup>143</sup> On the other hand phenolic portions were included by Brown<sup>144</sup> in rubber articles. Being more rigid than the latter, they aided in screwing the objects to supports. Fibrous inlays have been molded into articles which it was desired subsequently to glue to wooden backings.<sup>145</sup> Oving-

<sup>128</sup> J. R. Gammeter, U. S. P. 1,792,083, Feb. 10, 1931, to G. W. Perks Co.; *Chem. Abs.*, 1931, 25, 1963.

<sup>129</sup> The term "insert" is usually not applied to inlays or to forms around which the plastic composition is molded. It refers rather to relatively small sockets and projecting pieces, e.g., binding posts and electrical contacts, which are molded *in situ*.

<sup>130</sup> F. S. Kochendorfer, U. S. P. 1,720,681, July 16, 1929, to Western Electric Co., Inc.; *Chem. Abs.*, 1929, 23, 4308. W. A. Schmittgen, U. S. P. 1,728,218, Sept. 17, 1929, to General Industries Co.; *Chem. Abs.*, 1929, 23, 5283.

<sup>131</sup> H. J. Kasch, U. S. P. 1,811,086, June 23, 1931, to Kurz-Kasch Co. See also L. J. Norton and C. J. Willett, British P. 351,165, 1930; *Chem. Abs.*, 1932, 26, 4426. Cf. the molding of irregularly shaped objects around fibrous inserts. K. Brown, U. S. P. 1,308,330, July 1, 1919.

<sup>132</sup> L. H. Baekeland, U. S. P. 1,160,364, Nov. 16, 1915; *Chem. Abs.*, 1916, 10, 257.

<sup>133</sup> E. E. Novotny, U. S. P. 1,398,145, Nov. 22, 1921, to J. S. Stokes; *Chem. Abs.*, 1922, 16, 803. See also J. P. Wright, U. S. P. 1,438,078, Dec. 5, 1922; *Chem. Abs.*, 1923, 17, 860.

<sup>134</sup> D. N. Davies, British P. 327,728, 1929, to Bakelite, Ltd.; *Chem. Abs.*, 1930, 24, 5120.

<sup>135</sup> L. T. Frederick, U. S. P. 1,636,410, July 19, 1927, to Fibroc Insulation Co.

<sup>136</sup> V. G. Apple, U. S. P. 1,132,297, Mar. 16, 1915, to Apple Elec. Co.

<sup>137</sup> C. Zenk, U. S. P. 1,046,928, Dec. 10, 1912. C. Zenk, U. S. P. 1,265,681, Feb. 5, 1918, to Diehl Mfg. Co. L. T. Frederick and L. McCulloch, U. S. P. 1,231,588, July 3, 1917, to Westinghouse Elec. & Mfg. Co. H. M. Scheibe, U. S. P. 1,241,559, Oct. 2, 1917, to Westinghouse Elec. & Mfg. Co. E. A. Halbleib and T. L. Lee, U. S. P. 1,274,411, Aug. 6, 1918; *Chem. Abs.*, 1918, 12, 1950.

<sup>138</sup> J. A. McKee, R. S. Scott and R. A. McKee, British P. 421,053, 1933; *Brit. Chem. Abs. B*, 1935, 158.

<sup>139</sup> F. Groff, U. S. P. 1,977,876, Oct. 23, 1934, to Bakelite Corp.; *Chem. Abs.*, 1935, 29, 252. British P. 367,045, 1930; *Brit. Chem. Abs. B*, 1932, 437.

<sup>140</sup> See Chapter 19.

<sup>141</sup> See also Chapter 68.

<sup>142</sup> Le Bonheur, U. S. P. 1,686,142, Oct. 2, 1928; *Chem. Abs.*, 1928, 22, 4739.

<sup>143</sup> E. C. Ballman, U. S. P. 1,636,798, July 26, 1927; *Plastics*, 1928, 4, 138.

<sup>144</sup> K. Brown, U. S. P. 1,250,953, Dec. 25, 1917, to Condensite Co. of Amer.

<sup>145</sup> S. Brown, U. S. P. 1,524,335, Jan. 27, 1925, to Bakelite Corp.; *Chem. Abs.*, 1925, 19, 1036.

ton<sup>146</sup> proposed making a bearing for chromium-plated steel shafts from hardened phenol-formaldehyde resins faced with glass.

**Castable Resins.** The materials made by the early investigators of the phenolic resins left much to be desired in the matter of color and what is called tooling or machining. Therefore, much work was done in order to secure a condensation product that would not change in color with time and that could be machined or cut with the tools that were satisfactory on horn, vegetable ivory and related raw materials. The production of an article capable of being worked on a lathe or automatic screw-machine was fraught with difficulties because of the inherent brittleness and hardness of the resins. So great has been the progress in this direction that today we have a group of resins which are known as the turnery stock and which are available in a wide range of colors and shades. Such articles as chess pieces, checker men, buttons, bracelets, anklets, bases for lamps, door knobs, automobile gear-shift knobs and beads are made in a considerable annual tonnage. One advantage of casting is that it is the only recognized method which permits of the preparation of transparent objects from phenolic condensation products. In hot molding, cloudy products result due partly to incomplete fusion of the particles composing the powder.<sup>147</sup>

Even with casting, transparency is an elusive property. Absolute control during the condensing operation is most difficult; and, although a seeming uniformity is obtained by mixing batches, it was and is a great problem to make light-colored resins. Removing water during or after the preliminary condensation stage is also a serious obstacle and it is often necessary to check the reaction by dilution with organic solvents when dehydration nears completion. This frequently brings about incomplete reaction, and in consequence uncombined reagents are present in the finished product. Chief among these are water, alkali catalyst, phenol and aldehyde, all of which are to a degree destructive of transparency and usually render the material worthless for casting glass-clear masses.

A number of different means have been employed to obtain translucent and tough bodies. For example, condensation in the presence of salicylic acid followed by neutralization with a volatile amine and distillation *in vacuo* has been suggested.<sup>148</sup> Wennagel<sup>149</sup> proposed to use alkali soaps in proportions greater than one-fifth the molecular equivalent of the phenol as condensing agents. Deutsch and Thorn carried the reaction out in the presence of sodium carbonate and added salts of boric<sup>150</sup> or phosphoric acid<sup>151</sup> to render harmless the impurities which discolored the product. Acidification with acetic acid was stated to make the clarification more permanent. The same investigators report that, if salts of aromatic acids are added, the removal of water need not be as complete as it must otherwise be in order to obtain transparent resins.<sup>152</sup> The addition of sodium glycerate to toughen the product was advocated by Heinemann.<sup>153</sup>

The material known as "Catalin"<sup>154</sup> is of the cast phenol-formaldehyde type.

<sup>146</sup> E. J. Ovington, U. S. P. 1,930,081 and 1,980,082, Nov. 6, 1934, one-half to C. L. Dawes; *Chem. Abs.*, 1935, 29, 256.

<sup>147</sup> D. A. Spencer and H. D. Murrav, *J.S.C.I.*, 1927, 46, 637. *Cf.* the preparation of daylight filters colored with metal salts. H. Weiss, *British P.* 215,752, 1924; *J.S.C.I.*, 1924, 43, 665B.

<sup>148</sup> Austrian P. 102,677, 1921, to Resan Kunstharzerzeugungs-G. m. b. H.; *Brit. Chem. Abs. B.*, 1926, 890.

<sup>149</sup> T. S. Wennagel, U. S. P. 1,107,003, Aug. 11, 1914; *Chem. Abs.*, 1914, 8, 3377. *Cf.* U. S. P. 1,197,316, Sept. 5, 1916; *Chem. Abs.*, 1916, 10, 2969.

<sup>150</sup> L. Deutsch and I. Thorn, U. S. P. 1,678,107, July 24, 1928, to Selden Co.; *Chem. Abs.*, 1928, 22, 3498. *British P.* 207,792, 1923, to "Amalith" chem. Ind. G.m.b.H.; *J.S.C.I.*, 1923, 44, 216B.

<sup>151</sup> L. Deutsch and I. Thorn, U. S. P. 1,710,045, April 23, 1929, to Selden Co.; *Chem. Abs.*, 1929, 23, 2793. *British P.* 207,792, 1923, to "Amalith" chem. Ind. G.m.b.H.; *J.S.C.I.*, 1923, 44, 216B.

<sup>152</sup> L. Deutsch and I. Thorn, U. S. P. 1,710,019, Apr. 23, 1929, to Selden Co.; *Chem. Abs.*, 1929, 23, 2841. *British P.* 207,791, 1923, to "Amalith" chem. Ind. G.m.b.H.; *J.S.C.I.*, 1923, 44, 216B.

<sup>153</sup> A. Heinemann, U. S. P. 1,441,981, Jan. 9, 1923; *Chem. Abs.*, 1923, 17, 1137. *British P.* 184,984, 1921; *Chem. Abs.*, 1923, 17, 218.

<sup>154</sup> Catalin Corp. of America, New York, N. Y. For litigation, see *Chem. Ind.*, 1934, 34, 442.

Pantke<sup>156</sup> has prepared clear masses in accordance with the following general procedure:

Phenol is mixed with commercial formaldehyde, and either caustic potash or soda is used as a catalyst. Extreme care is taken to select very pure raw materials if light shades are to be produced. The mixture is heated in an aluminum or nickel vessel under non-refluxing conditions at a relatively low temperature (not in excess of 80°C.) until water separates. Then the water is removed under vacuum and lactic acid<sup>156</sup> (U. S. P. quality) is added together with a small amount of glycerol.<sup>157</sup> The latter serves as a plasticizer as well as a modifier. Further heating at a low temperature carries the resinification to the desired point, as evidenced by drawing a sample and dropping a small portion into a beaker of water at 15°C. When it chills to a pasty mass just kneadable between the fingers, the resin is ready for casting into molds, which have been previously made by dipping hard steel arbors into molten lead (an antimonial lead) and then withdrawing the arbor by a slight shock. These molds are kept warm and when resin and mold are in proper condition the former is withdrawn from the kettle in hand-dippers and poured into the molds which have previously been racked on a truck. Extreme care is used in pouring in order that air bubbles are not left in the material. The truck is now wheeled into heated chambers (erroneously called "vulcanizers") and the casting is allowed to cure. After 2 or 3 days depending on the desired hardness, the truck is removed and the resin is punched out of the molds with air-hammers. The lead molds are scrapped and remelted.

The above procedure yields a nearly colorless resin capable of being machined with ordinary tools. It can be sanded, polished and in general compares to brass and the hard woods in workability.<sup>158</sup> Variations are accomplished by leaving in a percentage of water, addition of pigments, dyestuffs or inert fillers. The simulation of precious stones that is possible with this material is quite remarkable.

A number of modifications of the general procedure given above have been proposed. Pollak and Ostersetzer<sup>159</sup> stated that care should be taken lest the resin separate from the water. According to them, it was desirable to have the product in the form of a gel. A large proportion (about 2½ mols to 1 of phenol) of formaldehyde was also used.<sup>160</sup> If transparent resins were to be made, acids which would give soluble salts with the bases used in the initial condensation were employed.<sup>161</sup> On the other hand, Loos<sup>162</sup> produced cloudy effects resembling marble by precipitating potassium acid tartrate throughout the mass. The addition of phenol in several portions during the course of the reaction has been reported to assist in keeping the resin in solution<sup>163</sup> and to result in a body which does not contain any free formaldehyde.<sup>164</sup> The latter end can also be attained by adding

<sup>156</sup> O. Pantke, U. S. P. 1,909,786, May 16, 1933, to Catalin Corp. of Am.; *Chem. Abs.*, 1933, 27, 3837. See also W. Peterson and E. V. Clark, British P. 179,586, 1921; *Chem. Abs.*, 1922, 16, 3531.

<sup>157</sup> O. Pantke (U. S. P. 1,909,788, May 15, 1933, to Catalin Corp. of Am.; *Chem. Abs.*, 1933, 27, 3837) states that an imitation ivory can be obtained using technical lactic acid. Cf. the preparation of a resin (to be used in dentures) in which oxalic acid is added, British P. 359,424, 1930, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 434.

<sup>158</sup> Omitting the glycerol produces a material resembling marble. O. Pantke, U. S. P. 1,909,789, May 16, 1933, to Catalin Corp. of Am.; *Chem. Abs.*, 1933, 27, 3837. If 0.25-0.35 part of glycerol to 1 part of phenol and 0.8 part of formaldehyde are used, the product is transparent. O. Pantke, U. S. P. 1,909,787, May 16, 1933, to Catalin Corp. of Am.; *Chem. Abs.*, 1933, 27, 3837.

<sup>159</sup> However, K. Raschig and M. Koebner (U. S. P. 1,934,817, Nov. 14, 1933, to F. Raschig G. m. b. H.; *Chem. Abs.*, 1934, 28, 664) recommend casting the resin on a block of wood which can be firmly clamped in cutting machines.

<sup>160</sup> F. Pollak and A. Ostersetzer, U. S. P. 1,854,600, April 19, 1932, to Pollopos, Ltd.; *Chem. Abs.*, 1932, 26, 3344. British P. 267,901, 1927, to Kunstharzfabr. F. Pollak G.m.b.H.; *Brit. Chem. Abs. B.*, 1928, 720.

<sup>161</sup> Cf. British P. 357,276, 1930, to Kunstharzfabr. F. Pollak G.m.b.H.; *Brit. Chem. Abs. B.*, 1931, 1107.

<sup>162</sup> A. Ostersetzer and F. Riesenfeld, U. S. P. 1,858,168, May 10, 1932, to Pollopos, Ltd.; *Chem. Abs.*, 1932, 26, 3945. British P. 290,963, 1927, to Kunstharzfabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1929, 23, 1294. French P. 653,354, 1928; *Chem. Abs.*, 1929, 23, 3822.

<sup>163</sup> K. Loos, U. S. P. 1,960,116, May 22, 1934; *Chem. Abs.*, 1934, 28, 4548.

<sup>164</sup> French P. 703,281, 1930, to "Herold" A.-G.; *Chem. Abs.*, 1931, 25, 4422.

<sup>165</sup> A. Ostersetzer and F. Riesenfeld, U. S. P. 1,892,848, Jan. 3, 1933, to Pollopos, Ltd.; *Chem. Abs.*, 1933, 27, 2259.

urea at the end of the condensation.<sup>165</sup> Jäger<sup>166</sup> employed sodium stearate and sodium sebacate as initial condensing agents. He also states that colorless products are obtained by adding such salts of strong organic bases as piperidine pentamethylenedithiocarbamate to a phenol-formaldehyde-ammonia reaction-mixture before or after condensation.<sup>167</sup>

In accordance with the methods outlined, artificial jewelry, handles for knives and umbrellas, cabinets, high-tension insulators<sup>168</sup> and a large number of similar objects have been manufactured. The purification of clear transparent resins has also attracted attention. Surfaces which have become matt or discolored by exposure to light or air may be rendered glossy by treatment with nitrogen-free carbocyclic or heterocyclic liquids such as dioxane, cyclohexanone or cyclohexanol.<sup>169</sup>

A proposed application of such transparent bodies is the construction of models to be used in photo-elasticity tests.<sup>170</sup> When the models are viewed with polarized light, they appear to be differently colored depending on the degree of stress. In this way, quantitative measurements of the distribution of load in such structures as the frame of a dirigible may be made. A viewing-polariscope for selection of material free from initial strains may be made as follows. It can be used of course on any transparent object (lamp shades, castings, films or composite sheets of safety glass) as well as on material for model construction.

A suitable light source for a viewing-polariscope may be a board about a foot square on which a number of electric light bulbs have been mounted. Directly below this is a sheet of glass having both sides sanded or a ground glass surface. This acts as a source of diffused light so that the filaments of the bulbs are not really visible through it. A piece of black glass about 12 inches x 18 inches is set directly below the ground glass surface so that it is inclined to the vertical rays of light from the ground glass surface at an angle of about 45° and arranged to reflect the light horizontally toward the left. This polarizes the light coming from the ground glass surface by reflection in a given plane.

A second piece of black glass is then placed so that it is at an angle of 45° to the light reflected from the first black reflecting surface and so that the reflected light will come directly out horizontally toward the observer and at right angles to the rays coming from the first reflecting surface. Two black sheets of laminated phenolic material will work very nicely as these two reflecting surfaces instead of the black glass. Highly polished metal surfaces would also be satisfactory, but ordinary mirrors with silvered surfaces cannot be used on account of reflection from both the front and back of the glass. The reflecting surfaces would function best if they were arranged so as to be at the critical angle with respect to the incident light beam, but the 45° arrangement will function quite satisfactorily and is much easier to set up and use.

The sheet of material to be studied is placed with its plane at right angles to the light beam upon its reflection from the first reflecting surface and before the light falls upon the second reflecting surface. The observer looks into the second reflecting surface, getting in the line of the reflected rays from that surface. By rotating the sheet of material with its plane perpendicular to the incident polarized rays around the line of the incident rays as an axis, the positions of strains in the sheet can be readily located as they will cause colored bands to appear during the rotation.

It has been stated above that accurate shapes cannot be made by casting. However, in some cases where hot molding is impracticable or where accuracy of

<sup>165</sup> H. L. Bender, U. S. P. 1,944,143, Jan. 16, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 2137. British P. 349,521, 1930; *Brit. Chem. Abs. B*, 1931, 729.

<sup>166</sup> A. Jäger, British P. 281,537, 1927, to "Herold" A.-G.; *Brit. Chem. Abs. B*, 1928, 101. French P. 666,184, 1928; *Chem. Abs.*, 1930, 24, 1476.

<sup>167</sup> A. Jäger, British P. 341,083, 1929, to "Herold" A.-G.; *Brit. Chem. Abs. B*, 1931, 405. German P. 496,730, 1927; *Chem. Abs.*, 1930, 24, 3662.

<sup>168</sup> British P. 303,883, 1928, to Rheinisch-Westfälische-Sprengstoff-A.-G. vorm W. Laymeyer & Co.; *Chem. Abs.*, 1929, 23, 4515.

<sup>169</sup> German P. 550,552, 1929, to "Herold" A.-G.; *Chem. Abs.*, 1932, 26, 4970. See also A. Osterseizer and F. Riesenfeld, German P. 549,886, 1929, to Rheinisch-Westfälische-Sprengstoff-A.-G.; *Chem. Abs.*, 1932, 26, 4925.

<sup>170</sup> Z. Tuzi, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, 1927, 7, 79. I. Arakawa, *Proc. Phys.-Math. Soc. Japan*, 1925, (3) 7, 160. R. V. Baud, *J. Optical Soc. Am.*, 1929, 18, 411, 422. R. B. Carleton, *U. S. Sci. Instruments*, 1934, 5, 80. J. H. A. Brahts, *ibid.*, 1934, 5, 80. *India Rubber J.*, 1933, 86, 53.

detail is not needed,<sup>171</sup> casting has been employed as a means of shaping. Thus, Wirth<sup>172</sup> formed pasty masses of phenolic resins filled with acid-resistant materials, e.g., asbestos, in open molds similar to those used with concrete. Hardening was then effected by applying heat. Objects manufactured in this way were somewhat porous and the surface was covered with a dense crust. The latter had to be removed by grinding or sand-blasting before the temperature was raised above 130°C. or blistering would occur. The articles were finally heated to 200°C. or more. With large pieces, the heating took at least 30-70 hours. Cylinders measuring 2 m. high, 2 m. in diameter and 4 cm. in thickness and other types of castings have been made in this way.<sup>173</sup>

Tubes may be pressed from phenol-formaldehyde resins both in the cold<sup>174</sup> and at elevated temperatures.<sup>175</sup> In the former case, the hardening of the resin is accomplished by passing hot air through the tube, producing a dense inner surface. Rods can be made in similar manner.

A phenolic composition which can be cold molded has been prepared by Ellis.<sup>176</sup> One hundred parts of o-cresol, 50<sup>177</sup> parts of paraform and 4 parts of aqueous caustic soda solution (30 per cent) were heated for 3½ hours on a vigorously boiling water bath. A reddish turbid solid resin was obtained which was soft at first but on standing a few hours became brittle. Asbestos fiber (75 parts) was impregnated with an acetone solution of the resin (20 parts) and tung oil (2 parts). The mass was spread in thin layers and dried at 70°C. for about 1 hour. It could then be shaped in a press at a pressure of 15,000 pounds per square inch and hardened by baking in an oven. The temperature was raised slowly from 60°C. to above 100°C. and then more rapidly to 140°C. Disks made in this way had a breaking-strength of 7 pounds per mm. of thickness.

Ariente and Flick<sup>177</sup> applied drops of liquid phenolic resins to fabric and completed the condensation by heating. It is stated that this method of decorating is better than similar ones used previously in that the globules<sup>178</sup> were neither soluble nor thermoplastic. Articles can also be made by electrodepositing the resin from aqueous dispersion on a mold surrounding the anode, followed, as in the other cases where the shaping is done in the cold, by baking.<sup>179</sup>

#### LAMINATED MATERIALS

In the electrical field, it was formerly common practice to coat paper with varnish or solutions of natural resins and to compact the sheets into a solid block by hot pressing. Shellac, copal and other natural resins have all been used. Copal and shellac yield pressboard which possesses good mechanical and electrical properties when cold but which softens when heated to 70-90°C. Therefore, the

<sup>171</sup> Cf. the manufacture of grinding wheels by shaping abrasive grains coated with a resin followed by baking while still in the mold. A. J. Doermann, U. S. P. 1,755,437, Dec. 16, 1930; *Chem. Abs.*, 1931, 25, 573. U. S. Reissue 13,373, June 20, 1933; *Chem. Abs.*, 1933, 27, 4369. W. L. Howe and R. H. Martin (U. S. P. 1,933,032, Dec. 4, 1934, to Norton Co.; *Chem. Abs.*, 1935, 29, 570) proposed to allow for shrinkage by adjusting the proportions of ingredients in the mixture to give predetermined volume percentages of abrasive, bonding agent and pores.

<sup>172</sup> J. H. Wirth, U. S. P. 1,917,413, July 11, 1933; *Chem. Abs.*, 1933, 27, 4702. German P. 477,836, 1926, to Säureschutz G.m.b.H.; *Chem. Abs.*, 1929, 23, 4357. Cf. E. Elbel, German P. 533,289, 1927, to Bakelite G.m.b.H.; *Chem. Abs.*, 1932, 26, 611.

<sup>173</sup> Mention is made above (in connection with the use of asbestos as a filler) of several other types of apparatus made of Havez (see page 458).

<sup>174</sup> French P. 707,214, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 815.

<sup>175</sup> H. C. Egerton, U. S. P. 1,370,800, Mar. 8, 1921; *Chem. Abs.*, 1921, 15, 1739.

<sup>176</sup> Carleton Ellis, U. S. P. 1,645,693, Oct. 18, 1927; *Chem. Abs.*, 1928, 22, 174. See also French P. 715,023, 1931, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 1731. Cf. French P. 691,896, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 1400.

<sup>177</sup> P. J. Ariente and L. Flick, U. S. P. 1,495,146, May 27, 1924, to Sayles Finishing Plants, Inc.; *Chem. Abs.*, 1924, 18, 2255.

<sup>178</sup> Cf. the formation of small spheres by a pair of rotating spindles, Austrian P. 95,867, 1924, to Schickelans & Co.; *Kunststoffe*, 1925, 15, 45.

<sup>179</sup> R. C. Davies, British P. 291,477, 1928, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs. B*, 1928, 614.

mechanical and (to a large extent) the electrical strength are lost when a temperature of 80°C. is reached. Such temperature conditions are of course not unlikely under service conditions in many types of electrical apparatus. As soon as the manufacture of phenol-formaldehyde resins became developed commercially, they were employed for the manufacture of laminated pressboard.<sup>120</sup> The mechanical strength of such pressboard does not decrease with increase in temperature to nearly as great an extent as does that of material made from natural resins.

Phenol-formaldehyde resins have also found wide use as a coating or impregnant for canvas and fiber. As a dielectric, dry fiber is ideal in many ways, but its tendency to absorb water affects its properties. Impregnating and binding together the fibers with a resin greatly reduces this tendency.<sup>121</sup> However, the reaction taking place when phenol-formaldehyde resins undergo hardening develops water and the presence of this reduces the dielectric strength. Great progress has, however, been made in the production of such pressboard and it is now being used for purposes where only the best insulators can be employed, e.g., wireless apparatus and electric railway track insulation.<sup>122</sup> Impregnated canvas is used more for mechanical than electrical purposes. It finds employment in the manufacture of noiseless gears, airplane propellers and in numerous other ways.<sup>123</sup>

The usual method of impregnating fabric is to use a solution of resin (in the A stage) through which a web of the material is passed continuously. The varnish-laden sheet then goes to a drier (usually of the tower type) where the solvent is evaporated.<sup>124</sup> If 1.5-3 per cent (based on the solid content) of tung oil is added to the solution, the resulting film will be more coherent.<sup>125</sup> A further modification involves washing the partially dried fabric with water or dilute alkali to effect removal of any compounds which produce objectionable odors.<sup>126</sup> However, other means similar to those which were mentioned for preparing molding compositions can be employed. That is, a liquid condensation product may

<sup>120</sup> Cf. the use of phenolic condensation products as adhesives in uniting wood and paper. R. W. Seabury, U. S. P. 1,625,749, April 19, 1927; *Chem. Abs.*, 1927, 21, 2054.

<sup>121</sup> For discussions of the hygroscopic tendencies of phenol-formaldehyde resins, see W. Gnann, *Z. Physik.*, 1930, 66, 436; *Chem. Abs.*, 1931, 25, 2037. H. G. Leopold and J. Johnston, *J. Phys. Chem.*, 1928, 32, 876; *Chem. Abs.*, 1928, 22, 3080.

<sup>122</sup> Studies on the electrical properties of phenolic-resin laminated material have been carried out by C. Hecker and E. H. Ott, *Raw Material*, 1921, 4, 449; *Chem. Abs.*, 1922, 16, 977. H. Clark, *Phys. Rev.*, 1924, 23, 652; *Chem. Abs.*, 1925, 19, 3214. L. Kumlik, *Elektrizitätswirtschaft*, 1928, 27, 423; *Chem. Abs.*, 1929, 23, 1575. S. G. Brown and P. A. Sporing, *Electrician*, 1929, 102, 443; *Chem. Abs.*, 1929, 23, 3032. *J. Inst. Elec. Eng. (London)*, 1929, 67, 968, 985, 990; *Chem. Abs.*, 1929, 23, 4681. K. Atsuki and K. Mat-suoka, *J.S.C.I. (Japan)*, 1930, 33, 387B; *Brit. Chem. Abs. B*, 1931, 479. A. Bültemann, *Kunststoffe*, 1922, 12, 66, 76. For the British standard specification on synthetic-resin varnish-paper boards and tubes for general electrical purposes excluding tubes molded after being rolled, see *Brit. Eng. Standards Assoc.*, 1929, 316; *Chem. Abs.*, 1929, 23, 3522.

<sup>123</sup> Laminated products employing a phenol-formaldehyde-resin binder are prepared in a number of grades by the following companies:

Company	Trade Name	Base
Continental Fibre Co. ....	"Bakelite Dilecto"	Paper or Fiber
Diamond State Fibre Co. ....	"Continental Bakelite"	Canvas
Formica Insulation Co. ....	"Condensite Celoron"	Fiber and Canvas
General Electric Co. ....	"Formica"	Paper and Canvas
Mica Insulator Co. ....	"Textolite"	
National Vulcanized Fibre Co. ....	"Lamicaid"	
Panelyte Corp. ....	"Phenolite"	
Spaulding Fibre Co. ....	"Panelyte"	
Synthane Corp. ....	"Spauldite"	
Westinghouse Elec. and Mfg. Co. ....	"Synthane"	
	"Bakelite Micarta"	Paper and Canvas

In Chapter 65, some of the methods which are generally applicable to the preparation of laminated material are described. The methods of testing such products are discussed in Chapter 69.

<sup>124</sup> J. P. Wright, U. S. P. 1,303,753, May 13, 1919; *Chem. Abs.*, 1919, 13, 1910. H. V. Potter (British P. 220,048, 1923, to Damard Lacquer Co., Ltd.; *Chem. Abs.*, 1925, 19, 739) employed as solvent methylated spirit containing 5-10 per cent of acetone. See also French P. 654,411, 1928, to I. G. Farbenbnd. A.-G.; *Chem. Abs.*, 1929, 23, 3568.

<sup>125</sup> G. H. Mains, U. S. P. 1,730,857, Oct. 8, 1929, and 1,841,138, Jan. 12, 1932, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1929, 23, 5600; *Chem. Abs.*, 1932, 26, 1731.

<sup>126</sup> G. H. Mains, U. S. P. 1,987,094, Jan. 15, 1935, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1935, 29, 1840.

be used in place of a solution<sup>190a</sup> or the binder may be prepared among the fibers of the material itself.<sup>197</sup> Weber<sup>188</sup> parchmentized paper with sodium hydroxide which later acted as a catalyst in the formation of the resin.<sup>189</sup> As with molding compositions, this procedure was stated to produce a more uniform and thorough impregnation. Another method which has been suggested is to sprinkle dry resin on a sheet of fibrous material which is then twisted into yarn and woven.<sup>190</sup> If a resorcinol condensation product is employed, the hardening of the pressboard

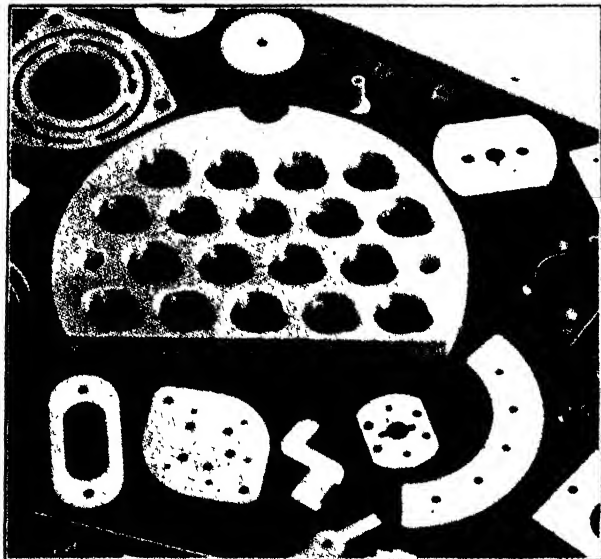


FIG. 78—Laminated Parts Fabricated with a Phenolic Type of Binder

Courtesy General Electric Co

will be more rapid. However, up to 50 per cent of this phenol may be replaced without unduly prolonging the process.<sup>191</sup>

There are three principal types of phenol-formaldehyde laminated sheets depending on the kind of fabric used in their manufacture. Paper is commonly used for electrical insulation,<sup>192</sup> but if greater strength is required linen and canvas are employed. Where high insulation value and resistance to moisture are of special importance, rag paper with about 50 per cent impregnation has been suggested. Hoey<sup>188</sup> proposed to use sheets which were alternately impervious and absorbent. Graduation in the dielectric constants of multiple cable insulation has

<sup>188a</sup> J. R. Wright, *loc. cit.* See also British P. 318,490, 1928, to H. Römmeler, A.-G.; *Chem. Abs.*, 1930, 24, 2217. British P. 357,204, 1930, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 1727.

<sup>187</sup> A. L. Brown, U. S. P. 1,695,912, Dec. 18, 1928, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1929, 23, 1002.

<sup>188</sup> H. C. P. Weber, U. S. P. 1,630,365, May 31, 1927, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1927, 21, 2363. H. C. P. Weber, U. S. 1,871,641, Aug. 16, 1932; *Chem. Abs.*, 1932, 26, 6081. British P. 169,451, 1921, to Metropolitan-Vickers Electrical Co., Ltd.; *J.S.C.I.*, 1922, 41, 978A.

<sup>189</sup> Cotton cloth has been rendered creaseless by impregnating in this manner after mercerization. R. P. Foulds, J. T. Marsh and F. C. Wood, British P. 291,474, 1927, to Tootal Broadhurst Lee Co.; *Brit. Chem. Abs. B*, 1928, 636. Formaldehyde-urea resins have also been suggested as anticrease impregnants. See Chapter 30.

<sup>190</sup> S. Brown and S. Higgins, U. S. P. 1,608,165, Nov. 23, 1926, to Bakelite Corp.; *Chem. Abs.*, 1927, 21, 307. Cf. the formation of clutch disks from previously impregnated asbestos yarn. H. Frood and W. H. Sydee, U. S. P. 1,604,985, Nov. 2, 1926. See also A. Winkler, British P. 394,495, 1932, to E. Esser & Co. G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 722.

<sup>191</sup> Allgem. Elektrizitäts-Ges., British P. 346,411, 1929, to Internat. General Elec. Co., Inc.; *Brit. Chem. Abs. B*, 1931, 627.

<sup>192</sup> For examples of the use in electrical insulation, see B. H. F. Richards and A. H. Haroldson, U. S. P. 1,897,651, Feb. 14, 1933, to Continental Diamond Fibre Co.; *Chem. Abs.*, 1933, 27, 2742. British P. 382,899, 1929, to Sprague Specialties Co.; *Chem. Abs.*, 1931, 25, 463.

<sup>188</sup> S. C. Hoey, U. S. P. 1,477,351, Dec. 11, 1923; *Chem. Abs.*, 1924, 18, 559.



been obtained by impregnating with solutions of different strengths.<sup>194</sup> Kraft paper<sup>195</sup> produces a stock which is resilient enough to be fashioned by punching. Further uses to which laminated paper has been applied are the manufacture of phonograph records<sup>196</sup> and damping-members for telephone diaphragms.<sup>197</sup> McIntosh<sup>198</sup> stated that a hard, tough waterproof product could be obtained from vulcanized fiber stock. A proposed wood substitute was built up from layers of pulp board.<sup>199</sup>

Phenol-formaldehyde linen-laminated sheet, because of the closely woven and uniform structure of the fabric layers, is especially adapted to the preparation of punched parts and the cutting of gears of small face dimension. It is stronger than paper and gives clean-cut, smooth edges. Canvas as a reinforcing material results in a sheet of maximum strength which can be used for the large gears

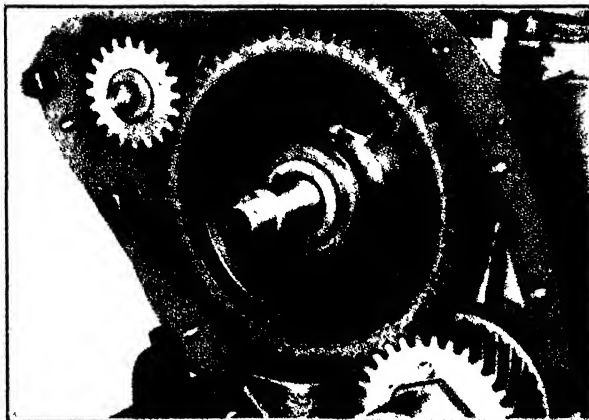


FIG 79—A Bakelite Laminated Gear in an Automobile Timing Mechanism.

*Courtesy Bakelite Corporation*

found in industrial machinery.<sup>200</sup> Such gears are more silent than metal ones and have demonstrated their ability to outlast metal in surroundings where corrosive solutions and abrasive dusts are encountered. In use, the laminated gears are arranged meshing with metal ones of at least equal width of face (see Fig. 79).

Conrad<sup>201</sup> simply cut gears from laminated stock. On the other hand, Bastian<sup>202</sup> punched the required shapes from impregnated sheets and then molded them together. The addition of graphite to self-lubricating gears has already been mentioned.<sup>203</sup> Another method impregnates the fabric with a non-drying oil previous to imbedding in the synthetic resin.<sup>204</sup> Metallic centers may also be included in

<sup>194</sup> British P. 251,931, 1925, to Felten & Guilleaume Carlswerk A -G.; *Chem. Abs.*, 1927, 21, 1505.

<sup>195</sup> H. L. Watson, British P. 284,232, 1923, to British Thomson-Houston Co.; *Brit. Chem. Abs.* B, 1929, 219.

<sup>196</sup> C. Bancarel, British P. 295,228, 1927; *Chem. Abs.*, 1929, 23, 2258

<sup>197</sup> H. F. Fruth, U. S. P. 1,833,642, Nov. 24, 1931, to Western Elec. Co.; *Chem. Abs.*, 1932, 26, 1080.

<sup>198</sup> J. McIntosh, U. S. P. 1,236,460, Aug. 14, 1917, to Diamond State Fibre Co.; *Chem. Abs.*, 1917, 11, 2949. See also E. E. Novotny and C. J. Romieux, U. S. P. 1,616,062, Feb. 1, 1927; *Chem. Abs.*, 1927, 21, 1010. Cf. F. F. Lucas, U. S. P. 1,470,990, Oct. 16, 1923; *Chem. Abs.*, 1924, 18, 137. G. E. Wightman, U. S. P. 1,996,314, Apr. 2, 1935

<sup>199</sup> British P. 291,633, 1927, to Agasote Millboard Co.; *Chem. Abs.*, 1929, 23, 1241.

<sup>200</sup> Reviews on laminated gears have been contributed by J. Rossman, *Plastics*, 1928, 4, 249, 268, 312, 332, 342, 433, 438; *Chem. Abs.*, 1928, 22, 3963.

<sup>201</sup> F. Conrad, U. S. P. 1,167,742, and 1,167,743, Jan. 11, 1916, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1916, 10, 812. The Conrad patents were held void for lack of invention, United States District Court, Southern District of Ohio, *Westinghouse Elec. & Mfg. Co. vs Formica Insulating Co.*, 270 Fed., 632; *Chem. Met. Eng.*, 1921, 25, 795.

<sup>202</sup> A. J. Bastian, U. S. P. 1,223,348, Apr. 17, 1917, to Westinghouse Elec. & Mfg. Co.

<sup>203</sup> L. T. Frederick, U. S. P. 1,564,774, Dec. 8, 1925; *Chem. Abs.*, 1926, 20, 484. See also section on graphite molding compositions.

<sup>204</sup> T. Sachs, British P. 400,172, 1933; *Chem. Abs.*, 1934, 28, 2483.

both gears<sup>205</sup> and abrasive wheels.<sup>206</sup> Sprenger<sup>207</sup> suggested that the teeth be formed of spirally wound cloth. Such a procedure would eliminate the waste inherent in cutting circular objects.<sup>208</sup>

Airplane propellers possessing a number of useful properties, including uniformity of texture, elasticity and absence of warping, have been made from laminated duck. Five or six sheets were formed together into a board, which was then shaped with a saw and finally molded under pressure at 175°C.<sup>209</sup> Woven fabrics have also been suggested for use in the manufacture of acoustic diaphragms,<sup>210</sup> billiard balls,<sup>211</sup> trays,<sup>212</sup> rayon-spinning pots<sup>213</sup> (see Fig. 80) and acid-proof receptacles.<sup>214</sup>

Stevenson<sup>215</sup> has recommended that the laminated sheet be built up of untreated cloth, then stitched or quilted together and finally impregnated. According to him, this procedure eliminated air pockets between the sheets and so resulted in a stronger body. The preparation of a non-laminated article by treating a specially woven fabric with a phenol-formaldehyde varnish has also been proposed.<sup>216</sup>

Asbestos sheets<sup>217</sup> have been used to make valve disks, gaskets and brake blocks.<sup>218</sup> According to Achtmeyer,<sup>219</sup> the employment of asbestos webbing in clutch facings is inconvenient since it tends to pucker when bent in a circle. On the other hand, sheets obtained by laying fibrous material in a paper machine are liable to break parallel with the fibers. The latter difficulty can be avoided by orienting the superimposed laminae at right angles to each other. Robertson<sup>220</sup> built up a friction material for use in brakes and clutches from alternate layers of asbestos fabric and granulated cork. Superposition of paper and layers of powdered glass is said to produce a body which is relatively bullet-proof.<sup>221</sup> Another form of laminated sheet has been made from flakes of mica bound with a phenol-urea-formalde-

<sup>205</sup> S. H. Thompson, U. S. P. 1,610,635, Dec. 14, 1926, to Westinghouse Elec. & Mfg. Co.

<sup>206</sup> B. Sanford, U. S. P. 1,881,970, Nov. 27, 1934, to Norton Co.; *Chem. Abs.*, 1935, 29, 570. Cf. the bonding of abrasive disks to a phenolic hub, D. E. Webster, U. S. 1,832,515, Nov. 17, 1931, to Norton Co.; *Chem. Abs.*, 1932, 26, 1088.

<sup>207</sup> R. Sprenger, U. S. P. 1,643,185, Sept. 20, 1927, to General Electric Co.

<sup>208</sup> Various schemes for cutting gears and wheels with a minimum of waste have been suggested. L. T. Frederick, U. S. 1,636,411, July 19, 1927 and 1,663,477, Mar. 20, 1928, to Fibroc Insulation Co.; *Chem. Abs.*, 1927, 21, 2965; 1928, 22, 1659. A. J. Bastian, U. S. P. 1,700,605, Jan. 29, 1929, to Westinghouse Elec. & Mfg. Co.; *Plastics*, 1929, 3, 391. E. J. Guay, U. S. P. 1,501,026, 1,501,027 and 1,501,028, July 8, 1924, to General Elec. Co. British P. 245,458, 1924, to Int. General Electric Co.; *Chem. Abs.*, 1927, 21, 307. See also S. Burgess, British P. 265,873, 1926; *Chem. Abs.*, 1928, 22, 1447. W. H. Adams, U. S. P. 1,708,166, Apr. 9, 1929; *Chem. Abs.*, 1929, 23, 2541.

<sup>209</sup> *J.S.C.I.*, 1920, 39, 338R. Cf. L. G. Nilson, U. S. P. 1,308,527, July 1, 1919. H. H. Semmes (U. S. P. 1,843,886, Feb. 2, 1932, to American Propeller Co.) cast phenolic propellers within reinforcing metal shells.

<sup>210</sup> J. H. Butcher and E. G. Crossling, British P. 255,582, 1925, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1927, 21, 2965. See also W. K. Webster, British P. 302,459, 1927; *Chem. Abs.*, 1929, 23, 4309. Cf. British P. 316,203, 1928, to N. V. Philips' Gloeilampenfabrieken; *Chem. Abs.*, 1930, 24, 1711.

<sup>211</sup> Allgem. Elektricitäts Ges. British P. 312,178, 1928, to Internat. General Elec. Co.; *Chem. Abs.*, 1930, 24, 929.

<sup>212</sup> British P. 346,412, 1929, to H. Römmeler A.-G.; *Chem. Abs.*, 1933, 27, 384.

<sup>213</sup> H. Jantgen, *Kunstseide*, 1926, 8, 295, 383; *Chem. Abs.*, 1927, 21, 648. A. P. Young, H. W. H. Warren and K. J. Chapman, British P. 293,060, 1927, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 23, 1805. F. Honda, British P. 361,064, 1930; *Chem. Abs.*, 1933, 27, 1171. See also E. Svatek, British P. 361,612, 1930; *Brit. Chem. Abs. B.*, 1932, 97.

<sup>214</sup> British P. 278,697, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 2476. See also G. A. E. Trombert, French P. 590,756, 1925; *Chem. Zentr.*, 1926, 1, 273.

<sup>215</sup> W. D. Stevenson, U. S. P. 1,295,230, Feb. 28, 1919; *Chem. Abs.*, 1919, 13, 1248.

<sup>216</sup> W. D. Stevenson, U. S. P. 1,392,535, Oct. 4, 1921; *Chem. Abs.*, 1922, 16, 502.

<sup>217</sup> C. A. Nash, British P. 341,941, 1928, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 2880. W. A. Jones, British P. 350,931, 1930, to Symantis Products, Ltd.; *Chem. Abs.*, 1933, 27, 576.

<sup>218</sup> W. Achtmeyer, U. S. P. 1,429,267, Sept. 19, 1922; *Chem. Abs.*, 1922, 16, 4023.

<sup>219</sup> W. Achtmeyer, U. S. P. 1,429,266, Sept. 19, 1922; *Chem. Abs.*, 1922, 16, 4023.

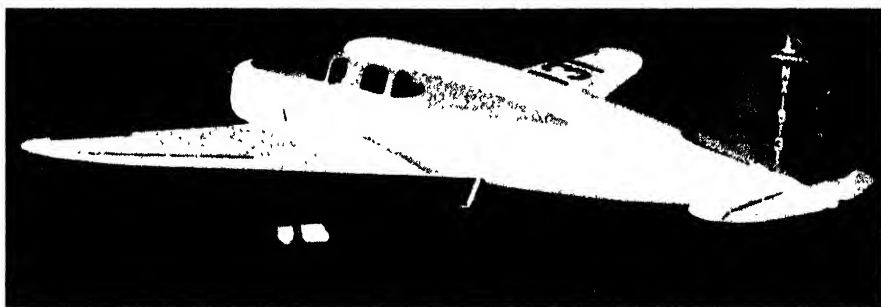
<sup>220</sup> J. H. Robertson, J. Robertson, Jr., and L. Gutteridge, British P. 368,765, 1930; *Chem. Abs.*, 1933, 27, 3048. See also W. C. Fisher, U. S. P. 1,436,158, Nov. 21, 1922; *Chem. Abs.*, 1923, 17, 618. Cf. the artificial leather made from layers of duck and cork, L. T. Frederick, U. S. P. 1,430,541, Oct. 3, 1922, to Westinghouse Elec. & Mfg. Co. British P. 399,886, 1933, to Behr-Manning Corp.; *Chem. Abs.*, 1934, 28, 1822.

<sup>221</sup> British P. 396,405, 1933, to General Elec. Co.; *Chem. Abs.*, 1934, 28, 1156.

hyde varnish.<sup>222</sup> McIntosh<sup>223</sup> proposed to make noiseless gears from layers of leather impregnated with a phenolic resin.

Wood-base Micarta is produced by saturating plywood and compacting a number of plies under a pressure of 1500 pounds per square inch and at a temperature of 140°C. One and a half hours is required for each inch of thickness and the material is allowed to cool to room temperature before removing from the press.<sup>224</sup> Oil-switch lift-rods constructed of such material are said by Read<sup>225</sup> to have breaking strengths superior to those made from natural materials.

**Rods and Tubes.** The usual method of making rods of laminated material is to machine them from sheet stock. Frederick<sup>226</sup> suggested that, if the condensation of the resin has not been carried to its final stage, rods can be molded from strips cut from a sheet. A method of making tubes is to wind laminated sheets around a core, remove the core, and cure the objects in a heated mold. Tubes are known as rolled or molded depending on whether heat and pressure are applied



Courtesy Bakelite Corp.

FIG. 80.—Fuselage and Wings of this Plane Are Made of Laminated Wood Bonded with a Phenolic Resin.

during the rolling<sup>227</sup> or afterwards in steel molds. In the latter case, the pressure may be applied either axially<sup>228</sup> or from the sides.<sup>229</sup> Kempton<sup>230</sup> has described a type of expanding mandrel which will apply the pressure from the inside of the tube. Standard sizes of such tubes include inside diameters of 3/16 inch to 72 inches and wall-thicknesses of 1/32 inch to 1½ inches.

<sup>222</sup> A. Lloyd, U. S. P. 1,784,737, Dec. 9, 1930, to Bakelite, Ltd.; *Chem. Abs.*, 1931, 25, 389. British P. 302,612, 1927; *Chem. Abs.*, 1929, 23, 4308. German P. 542,194, 1928; *Chem. Abs.*, 1932, 26, 2287.

<sup>223</sup> J. McIntosh, U. S. P. 1,269,292, June 11, 1918, to Diamond State Fibre Co.; *Chem. Abs.*, 1918, 12, 1843.

<sup>224</sup> J. R. Brossmann, U. S. P. 1,834,895, Dec. 1, 1931, to General Elec. Co.; *Chem. Abs.*, 1932, 26, 1092. J. R. Brossmann, British P. 387,183, 1933, to British Thomson-Houston Co.; *Chem. Abs.*, 1933, 27, 5446. See also J. R. Brossmann, British P. 402,677, 1933, to Brit. Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1934, 99. R. P. Jackson, G. C. Kent and E. J. Casselman, U. S. P. 1,628,886, May 17, 1927, to Westinghouse Elec. & Mfg. Co.

<sup>225</sup> E. N. Read, *Power*, 1929, 70, 646; *Chem. Abs.*, 1930, 24, 208. For a discussion of the various glues used in wood-working, see T. R. Truax, *Trans. Am. Soc. Mech. Engrs (Wood Industries)*, 1932, 54 (4), 1; *Chem. Abs.*, 1932, 26, 2616. A. Bresser, *Syn. and Appl. Finishes*, 1933, 4, 62; *Chem. Abs.*, 1934, 28, 3533. One of the proposed types of adhesive consists of cloth or paper sheets impregnated with phenolic resins. J. R. McClain, U. S. P. 1,299,747, Apr. 8, 1919, to Westinghouse Elec. & Mfg. Co. E. C. Loetscher, U. S. P. 1,891,430, Dec. 20, 1932; *Chem. Abs.*, 1933, 27, 2012.

<sup>226</sup> L. T. Frederick, U. S. P. 1,284,296, Nov. 12, 1918; to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1919, 13, 169.

<sup>227</sup> W. E. Boyle, U. S. P. 1,979,444, Nov. 6, 1934, to Spaulding Fibre Co.; *Chem. Abs.*, 1935, 29, 252. A. Aichele (U. S. P. 1,296,731, Mar. 11, 1919, to A.-G. Brown, Boverie & Cie) prepared an electrically insulating sleeve from laminated paper tubing.

<sup>228</sup> L. T. Frederick, U. S. P. 1,284,297, Nov. 12, 1918, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1919, 13, 169. W. N. Briggs, U. S. P. 1,631,668, Jan. 7, 1927, to General Elec. Co. British P. 263,878, 1926; *Chem. Abs.*, 1928, 22, 146.

<sup>229</sup> L. T. Frederick, U. S. P. 1,284,298, Nov. 12, 1918, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1919, 13, 169.

<sup>230</sup> W. H. Kempton, U. S. P. 1,284,363, Nov. 12, 1918, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1919, 13, 170.

In one method of making insulating tubes for coils of wire, a sheet of impregnated material is folded into a series of sharp parallel ribs and then cured in a mold of the same shape.<sup>251</sup> Tubes of desired size are made by cutting the sheets in proper widths and bending them into cylinders. The ribs give as little contact as possible between the tube and the wire wound on it.

**Veneers.** In some cases, it has been desirable to prepare articles in which the surfaces are different in composition from the body. Phenol-aldehyde insulators char when a spark passes over their surface with a resultant loss in resistance. Such is not the case with alkyd resins,<sup>252</sup> and so Barringer<sup>253</sup> has coated both moldings and laminated sheets with the latter substances to minimize the effect. Barrier rings for alternating-current motors have been made from a sheet of impregnated asbestos fabric between two rings of a wood-flour-filled molding composition. The former resisted flash-overs although the latter had a larger dielectric strength.<sup>254</sup> Valve disks having outside layers of asbestos fabric covering an inside mass of asbestos fibers have also been prepared.<sup>255</sup> Whitehouse<sup>256</sup> faced buttons of phenolic resin with celluloid. Nitrocellulose (additionally waterproofed by inclusion of a wax) and phenol-aldehyde condensation products were cast together on a cellulose acetate film<sup>257</sup> to form a duplex waterproof foil. The use of phenolic-resin impregnated veneers on a shellac-bonded sheet is stated by Cox<sup>258</sup> to avoid certain difficulties laid to the adhesive character of the shellac.

To cause cellulose-acetate-impregnated sheets to adhere to fibrous sheets impregnated with phenol resin, Worrell and Gruber<sup>259a</sup> employed a middle sheet impregnated with a mixture of phenol resin and cellulose acetate.

Phonograph records<sup>260</sup> were originally made from shellac and for many years this was the principal substance used. Its hardness and toughness and the simplicity of molding records containing it presented a hard problem to the synthetic-resin chemist seeking to produce a substitute. Aylsworth<sup>260</sup> devised a number of means of preparing a smooth hard layer of pure phenol-formaldehyde condensation product or one in which there was only a small quantity of filler and of affixing it on a supporting blank containing a larger amount of diluent. Usually the resin in the surface was relatively infusible, but contained some plasticizing agent.<sup>261</sup> The same investigator suggested that the body of a cylindrical record

<sup>251</sup> E. E. Novotny and F. W. Cary, U. S. P. 1,616,063, Feb. 1, 1927, to J. S. Stokes. See also B. H. F. Richards and A. H. Haroldson, U. S. P. 1,897,651, Feb. 14, 1933, to Continental Diamond Fibre Co.; *Chem. Abs.*, 1933, 27, 2742.

<sup>252</sup> See Chapter 69.

<sup>253</sup> L. E. Barringer, U. S. P. 1,915,969, June 27, 1933, to General Elec. Co.; *Chem. Abs.*, 1933, 27, 4605. British P. 387,066, 1931, to Brit. Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1933, 273. See also *Chem. Age (London)*, 1930, 23, 607.

<sup>254</sup> W. H. Kempton, U. S. P. 1,309,758, July 15, 1919, to Westinghouse Elec. & Mfg. Co.

<sup>255</sup> C. A. Nash, U. S. P. 1,888,179, Nov. 15, 1932, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 1465.

<sup>256</sup> J. N. Whitehouse, U. S. P. 1,881,038, Oct. 4, 1933; *Chem. Abs.*, 1933, 27, 575. Cf. the production of a composite electrical insulation from phenolic plastic and cellulose acetate, R. Burns, U. S. P. 1,911,803, May 30, 1933, to Bell Telephone Laboratories Inc.; *Chem. Abs.*, 1933, 27, 4000.

<sup>257</sup> G. A. Staley, British P. 356,146, 1930, to Non-Inflammable Film Co., Ltd.; *Brit. Chem. Abs. B*, 1931, 1045.

<sup>258</sup> G. R. Cox, U. S. P. 1,437,094, Nov. 28, 1922; *Chem. Abs.*, 1923, 17, 842. Cf. H. W. H. Warren, R. I. Martin and A. E. Smith, British P. 299,906, 1927, to Brit. Thomson-Houston Co.; *Chem. Abs.*, 1929, 23, 3524.

<sup>259a</sup> W. P. Worrell and F. E. Gruber, U. S. P. 1,998,827, Apr. 23, 1935, to Western Electric Co.

<sup>260</sup> For a review on the use of synthetic resins in phonograph records, see C. W. Rivise, *Plastics*, 1930, 6, 137.

<sup>260</sup> J. W. Aylsworth, U. S. P. 1,146,387, 1,146,390 and 1,146,391, July 13, 1915, to New Jersey Patent Co., *Chem. Abs.*, 1915, 9, 2432. J. W. Aylsworth and E. L. Aiken, U. S. P. 1,151,849, Aug. 31, 1915, to T. A. Edison, Inc.; *Chem. Abs.*, 1915, 9, 2799. J. W. Aylsworth, U. S. P. 1,167,468, Jan. 11, 1916, to New Jersey Patent Co.; *Chem. Abs.*, 1916, 10, 812. J. W. Aylsworth and E. L. Aiken, U. S. P. 1,170,391, Feb. 1, 1916, to New Jersey Patent Co.; *Chem. Abs.*, 1916, 10, 958. J. W. Aylsworth, U. S. P. 1,230,816, June 19, 1917, and 1,283,450, Nov. 5, 1918, to New Jersey Patent Co.; *Chem. Abs.*, 1919, 13, 170.

<sup>261</sup> Several plasticizers are mentioned above in connection with the work of Weber on hexamethylenetetramine-triphenol. See also Chapter 20 on modified phenol-formaldehyde resins.

be made of a composition which contained an excess of polymerized formaldehyde. On molding, this would be evolved in gaseous form producing a porous structure.<sup>242</sup>

Sound records were made by Novotny<sup>243</sup> from a fusible phenol-acetaldehyde resin. The condensation product was dissolved in alcohol to form a thin solution and hexamethylenetetramine was added. Sheets of fiber were impregnated and subsequently heated to remove solvents and partially react the resin, thus largely preventing side-flow during hot pressing. A plurality of sheets were cemented together with the resin solution and subjected to heavy pressure to insure firm adhesion. The product was coated with a thick paint composed of barium sulphate<sup>244</sup> and resin solution. Such blanks were heated at 120°C. for about 1 hour, coated a second time with the resin, dried to remove solvent and hot pressed in a record mold. Edison<sup>245</sup> recommended that a blank be coated with several layers of varnish instead of the two which previous workers had used.

A related material which can be employed for printing surfaces and stereotype matrices is made from a fibrous sheet which has been impregnated with a phenol-aldehyde condensation product. The sheet is heated until it is dry and crisp and the surfaces are then coated with several layers of phenol resin. Each layer is set by heating before the next is applied. The filler in the coatings is lampblack and the quantity used decreases progressively towards the surface.<sup>246</sup>

Playing cards have been similarly made by covering both sides of an impregnated linen sheet with phenol-formaldehyde resins. Such cards are reported as durable and possessing the requisite flexibility and finish.<sup>247</sup> A composite plate having veneers of impregnated parchmented paper and a center of plain parchmented stock is said to be less expensive than one uniformly saturated.<sup>248</sup> Loetscher<sup>249</sup> coated fiber board with a phenol-formaldehyde varnish and covered both sides with impregnated sheets of kraft paper. On the top surface a layer of powdered quartz coated with phenol resin was spread and the whole body was compressed under 50-100 pounds per square inch at a temperature high enough to fuse the binder. The finished product was used as a floor covering.

Table tops and similar articles of furniture were also made by pressing impregnated wood veneers around fibrous cores.<sup>250</sup> Such veneers are said not to be scorched by contact with matches or cigarettes.<sup>251</sup> Plywood reinforced with cloth can be molded over irregular surfaces.<sup>252</sup> Fire-resisting paneling having one or more

<sup>242</sup> J. W. Aylsworth, U. S. P. 1,043,389, Nov. 5, 1912, to T. A. Edison, Inc.

<sup>243</sup> E. E. Novotny, U. S. P. 1,440,097, Dec. 26, 1922, and 1,451,783, Apr. 17, 1923; *Chem. Abs.*, 1923, 17, 2035.

<sup>244</sup> The hard layer of barium-sulphate-filled plastic serves to prevent absorption of sound by the body of the record. E. E. Novotny, U. S. P. 1,398,144, Nov. 22, 1921, to J. S. Stokes; *Chem. Abs.*, 1922, 16, 803.

<sup>245</sup> T. A. Edison, U. S. P. 1,690,159, Nov. 6, 1923, to T. A. Edison, Inc.; *Chem. Abs.*, 1923, 23, 490. See also A. E. Alexander, British P. 176,828, 1920; *Chem. Abs.*, 1922, 16, 3177.

<sup>246</sup> A. E. Alexander, British P. 163,552, 1920; *Chem. Abs.*, 1922, 16, 146. See also E. E. Novotny, U. S. P. 1,398,142, and 1,398,143, Nov. 22, 1921, to J. S. Stokes; *Chem. Abs.*, 1922, 16, 803, 802.

<sup>247</sup> H. L. Pohns, U. S. P. 1,794,866, Mar. 3, 1931; *Chem. Abs.*, 1931, 25, 2255. M. R. Howard (U. S. P. 1,888,672, Nov. 22, 1932; *Chem. Abs.*, 1933, 27, 1511) employed paper stock in a similar card.

<sup>248</sup> J. M. Taylor, U. S. P. 1,441,133, Jan. 2, 1923, to Diamond State Fibre Co.; *Chem. Abs.*, 1923, 17, 1115.

<sup>249</sup> E. C. Loetscher, U. S. P. 1,825,877, Oct. 6, 1931; *Chem. Abs.*, 1932, 26, 577. See also H. C. Harvey and H. L. Becher, U. S. P. 1,763,653, June 17, 1930, 1,776,790, Sept. 30, 1930, and 1,851,177, Mar. 29, 1932, to Agasote Millboard Co.; *Chem. Abs.*, 1930, 24, 3903, 6016; 1932, 26, 3112. H. C. Fisher, U. S. P. 1,924,601, Aug. 29, 1933, to Richardson Co.

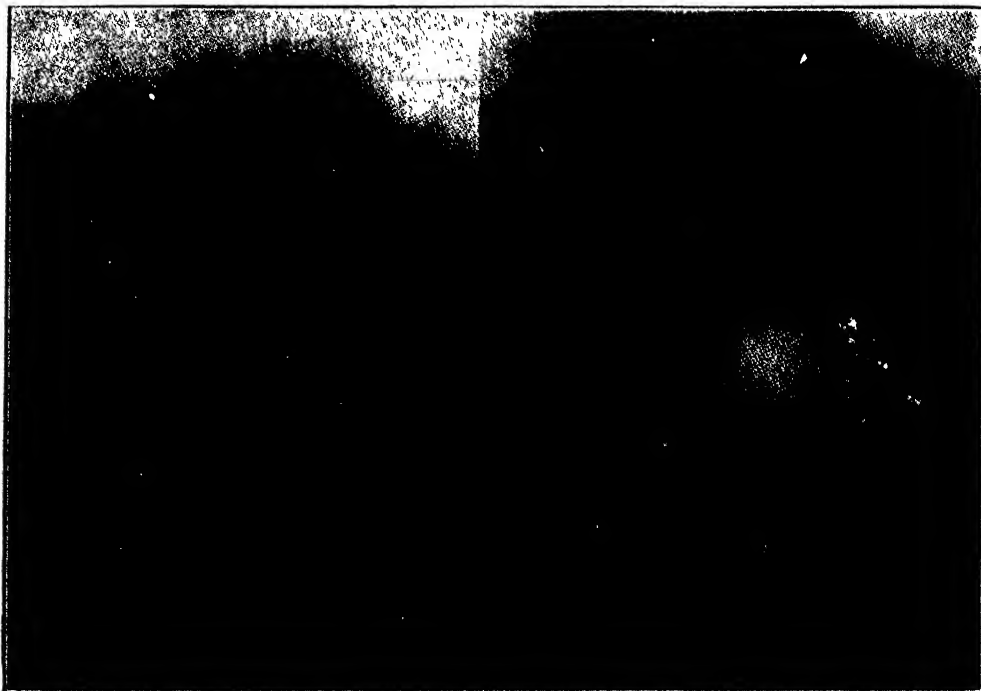
<sup>250</sup> E. C. Loetscher, U. S. P. 1,876,330, Sept. 6, 1932. See also F. H. Tupper, U. S. P. 1,637,362, Aug. 2, 1927, to Westinghouse Elec. & Mfg. Co.; *Plastics*, 1928, 4, 138. G. W. Bulley (U. S. P. 1,566,815, Dec. 22, 1925; *Chem. Abs.*, 1926, 20, 520) covered a hard rubber box with an impregnated wood veneer. Cf. the fibrous veneer on a metal-reinforced hard-rubber centrifuge bucket. J. R. Hiltner, U. S. P. 1,922,914, Feb. 26, 1935, to General Elec. Co.

<sup>251</sup> E. C. Loetscher, U. S. P. 1,887,691, Nov. 15, 1933; *Chem. Abs.*, 1933, 27, 1480.

<sup>252</sup> G. H. Mains, U. S. P. 1,959,762, May 22, 1934, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1934, 28, 4564. See also the preparation of paper tubes having wood veneers. G. H. Gardner, British P. 413,684, 1934, to Bushing Co., Ltd.; *Chem. Abs.*, 1935, 29, 344. To obtain good results in making plywood, using thermosetting resins as binders, the moisture content of the wood should be about 7-12

layers of asbestos between layers of wood was suggested by Gardner<sup>353</sup> (see Fig. 81). Other composite sheets which Loetscher has proposed consist of cellulose-fiber pulp covered with wood flour<sup>354</sup> and of interior layers of kraft paper, intermediate ones of wood flour and outer surfaces of thinner paper.<sup>355</sup>

Abrahams<sup>356</sup> covered phenol-aldehyde moldings with an insulating coating of mica bound with shellac. Like the alkyd resins mentioned above, shellac is not liable to tracking.<sup>357</sup> In the manufacture of laminated board containing layers of a



Courtesy Modern Plastics

FIG. 81.—Blowtorch Test Comparing Ordinary Plywood (right) and a Synthetic Resin Product. The center of the ordinary veneered door panel was completely destroyed after 30 minutes exposure. The other panel consists of a thin surface of wood backed with asbestos sheet impregnated with Durez resin. Exposure to the torch for 1½ hours merely charred the surface.

phenol-aldehyde resin-asbestos composition, rosin has also been included in the outer layers.<sup>358</sup> Vessels having a body of phenolic condensation product between metal shells are reported as minimizing temperature changes within the contents.<sup>359</sup>

per cent and the pressure should be released gradually in the pressing operation, according to C. B. Norris, U. S. P. 1,999,253, Apr. 30, 1935, to Reconstruction Finance Corp.

<sup>353</sup> G. H. Gardner, British P. 413,727, 1934, to Bushing Co., Ltd.; *Chem. Abs.*, 1935, 29, 531. Cf. the use of a surface layer impregnated with sodium silicate in a composite asbestos sheet. R. H. Cunningham, U. S. P. 1,960,180, May 22, 1934, to Bryant Elec. Co.; *Chem. Abs.*, 1934, 28, 4506.

<sup>354</sup> E. C. Loetscher, U. S. P. 1,875,054, Aug. 20, 1932; *Chem. Abs.*, 1932, 26, 6167.

<sup>355</sup> E. C. Loetscher, U. S. P. 1,938,917, Dec. 12, 1933; *Chem. Abs.*, 1934, 28, 1428.

<sup>356</sup> S. L. Abrahams, U. S. P. 1,693,327, Nov. 27, 1929, to General Elec. Co.; *Chem. Abs.*, 1929, 23, 678. Cf. the laminated material containing shellac in the outer layers. H. W. H. Warren, R. I. Martin and A. E. Smith, British P. 299,906, 1927, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 23, 3524.

<sup>357</sup> W. Nagel, *Metallbörse*, 1930, 20, 2133, 2190; *Chem. Abs.*, 1931, 25, 1107.

<sup>358</sup> S. O. Sinkov, Russian P. 8,866, 1929; *Chem. Zentr.*, 1931, 1, 1976.

<sup>359</sup> J. L. Leslie, U. S. P. 1,663,860, Mar. 20, 1928; *Chem. Abs.*, 1928, 22, 1686.

Thin sheets of metal,<sup>260</sup> onion-skin paper<sup>261</sup> or regenerated cellulose<sup>262</sup> have been used to face laminated stereotype matrices. Swan and Higgins<sup>263</sup> state that the insertion of a layer of vulcanized rubber cuts down the sound-transmission and increases the flexibility. Such material has been suggested for airplane cabins and cafeteria table tops. A backing of rubber has been used on printing plates of phenolic resin to minimize the danger of breaking.<sup>264</sup> Freeman and Catt<sup>265</sup> joined the fabric jacket of a rubber tube to the interior with phenolic cement. Asbestos sheets containing barium sulphate and bound with rubber or "Thiolite"<sup>266</sup> have been used as impervious layers on the outside of an asbestos-metal fabric gasket impregnated with a phenol condensation product.<sup>267</sup>

**Adhesives for Metals and Glass.** Phenolic resins have also been employed as adhesives for such substances as metals and glass which, of course, differ from the fabrics discussed above in that they possess relatively impervious structures. Investigations carried out by the Adhesive Research Committee<sup>268</sup> demonstrate that when saligenin is heated at about 130°C., the strength of the resulting adhesive increases progressively. After one hour, a phenol-formaldehyde type resin was obtained which was almost 7 times stronger than the original compound. The increase in strength was attributed to the disorderly structure which was assumed to be formed in resinification. A cement has been suggested in which neutral metallic oxides, aromatic sulphonyl chlorides or alkyl sulphates were added to a liquid phenol-formaldehyde condensation product to catalyze the hardening.<sup>269</sup> A resin for cementing glass and metals has been prepared by heating benzoic or cinnamic acid with glycerol, phenol and formaldehyde. The reaction product was dehydrated by vacuum distillation.<sup>270</sup> Warming a mixture of 40 parts of phenol, 100 parts of formaldehyde solution and 1.2 parts of sodium hydroxide for about 2.5 hours at 62°C. followed by treating with 3.3 parts of lactic acid and keeping at 60°C. until the mass is syrupy is said to produce a waterproof adhesive.<sup>271</sup> Aylsworth<sup>272</sup> dissolved 100 parts of fusible phenol resin in 100 parts of alcohol containing 20-50 parts of a nonvolatile solvent (monochloronaphthalene, glycerol or castor oil). Seven to eleven parts of hexamethylenetetramine and 50-300 parts of finely divided filler were also added. The material was intended to be used in sealing the joints of metal pipes. Veneers of paper and wood have been joined under heat and pressure to metal with water-soluble phenolic condensation products.<sup>273</sup> In electrical condensers the adhesive acts as a dielectric also.<sup>274</sup>

<sup>260</sup> H. Swan, U. S. P. 1,667,447, Apr. 24, 1928, to Bakelite Corp. See also W. Forstmann, P. K. Mensel and O. Boll, British P. 359,018, 1930; *Chem. Abs.*, 1932, 26, 4145.

<sup>261</sup> G. S. Williamson, U. S. P. 1,173,907, Feb. 29, 1916; *Chem. Abs.*, 1916, 10, 1084. See also L. H. Backeland, U. S. P. 1,233,298, July 17, 1917, to Gen. Bakelite Co.; *Chem. Abs.*, 1917, 11, 2604.

<sup>262</sup> H. Swan and S. Higgins, U. S. P. 1,960,602, May 29, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 4551.

<sup>263</sup> H. Swan and S. Higgins, U. S. P. 1,973,124, Sept. 11, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 6953.

<sup>264</sup> H. Swan and S. Higgins, U. S. P. 1,871,568, Aug. 16, 1932, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 6081.

<sup>265</sup> L. M. Freeman and H. W. Catt, U. S. P. 1,974,211, Sept. 18, 1934, to B. F. Goodrich Co.; *Chem. Abs.*, 1934, 28, 7072.

<sup>266</sup> See Chapter 59.

<sup>267</sup> H. Reins, U. S. P. 1,756,881, Apr. 29, 1930; *Chem. Abs.*, 1930, 24, 3092.

<sup>268</sup> *Chem. Age (London)*, 1932, 27, 167.

<sup>269</sup> French P. 723,008, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4142.

<sup>270</sup> H. Rösger, German P. 533,245, 1929; *Chem. Abs.*, 1932, 26, 611.

<sup>271</sup> L. C. F. Pechin, French P. 722,128, 1931; *Chem. Abs.*, 1932, 26, 4191.

<sup>272</sup> J. W. Aylsworth, U. S. P. 1,065,495, June 24, 1913, to Condensite Co. of Amer.; *Chem. Abs.*, 1913, 7, 2337. Cf. the inclusion of triphenyl or tritolyl phosphate. Patent-Treuhand-Ges. für elektr. Glühlampen, British P. 349,244, 1930, to General Elec. Co., Ltd.; *Brit. Chem. Abs. B*, 1931, 726.

<sup>273</sup> E. C. Loetscher, U. S. P. 1,972,307, Sept. 4, 1934; *Chem. Abs.*, 1934, 28, 6532. Another cement for veneers contains an aqueous suspension of phenol-aldehyde resin to which urotropine and fillers have been added. A. L. Eidlin, Russian P. 34,740, 1934; *Chem. Abs.*, 1935, 29, 3075.

<sup>274</sup> C. H. Stave, British P. 359,549, 1930; *Brit. Chem. Abs. B*, 1932, 28.

On the other hand some lack of success is encountered in affixing large sheets of phenol-formaldehyde resin to metal plates. Due probably to the differences in thermal expansion the two layers separate in time. A number of rubber cements<sup>275</sup> have been proposed to obviate this difficulty. Another method fastens an intermediate sheet of felt to a steel backing with a low-melting alloy.<sup>276</sup> Loetscher<sup>277</sup> reports that interposing a layer of paper saturated with phenol-formaldehyde-carbohydrate resin will also prevent separation.<sup>278</sup>

Double window panes have been formed by placing two sheets of glass at a slight distance apart and interposing along their edges an elastic filler, the surface of which had been previously coated with a phenolic condensation product. The latter was subsequently fused by raising the temperature.<sup>279</sup> Safety glass is made by uniting sheets of cellulose nitrate or acetate to exterior layers of glass.<sup>280</sup> In one way of using phenol-formaldehyde adhesives, glass is first polished with emery. A thick solution of the resin in acetone or alcohol is spread on at 30-40°C. with a spatula, and the temperature is raised to 80°C. to drive off the solvent. The sheets are then laid on top of each other and united by heating under about 5 atmospheres pressure.<sup>281</sup> To save solvent a melted resin can also be used.<sup>282</sup> It has been suggested to omit the layer of cellulose ester, but such products have not proven entirely satisfactory since the inclusion of the ester greatly strengthens the material. Long<sup>283</sup> reports that the union between glass surfaces has, if the resin layer is thin enough, a greater tensile strength than the glass itself. A further proposal reinforces glass objects with exterior coatings of phenolic resins.<sup>284</sup> One disadvantage which such condensation products have and which limits their use in safety glass is the tendency to darken on exposure to light.

Unbreakable transparent sheets to be used as a substitute for glass have been made by uniting two layers of celluloid with phenol-aldehyde resins.<sup>285</sup> Another glass substitute consists of gauze coated with an amount of phenolic resin insufficient to close the reticulations<sup>286</sup> and then with cellulose acetate filling the openings.<sup>287</sup> Keay<sup>288</sup> proposed to use a cement made of sand, phenol-formaldehyde resin

<sup>275</sup> H. Gray, U. S. P. 1,732,886, Oct. 22, 1929, to B. F. Goodrich Co.; *Chem. Abs.* 1930, 24, 265. German P. 432,485, 1923, to H. Traun & Sohne; *Brit. Chem. Abs.* B, 1927, 197. R. P. Courtney, U. S. P. 1,946,932, Feb. 13, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 2496. British P. 356,769, 1930; *Brit. Chem. Abs.* B, 1931, 1062. French P. 696,754, 1930; *Chem. Abs.*, 1931, 25, 2866. W. B. Wescott, U. S. P. 1,852,728, Apr. 5, 1932, to Rubber Latex Research Corp.; *Chem. Abs.*, 1932, 26, 3143.

<sup>276</sup> P. W. Jenkins and A. W. Coffman, *Plastic Products*, 1933, 9, 183. *Chem. Abs.*, 1933, 27, 4941.

<sup>277</sup> E. C. Loetscher, U. S. P. 1,972,307, Sept. 4, 1934, *Chem. Abs.*, 1934, 28, 6582.

<sup>278</sup> Similar sheets of paper impregnated with reactive synthetic resins have also been used to join surfaces of phenol-formaldehyde condensation products. Austrian P. 113,524, 1928, to Ambrasit-Werke Kunstharz-fabrik G.m.b.H.; *Chem. Abs.*, 1929, 23, 4357.

<sup>279</sup> E. Unmack, British P. 202,926, 1923; *Chem. Abs.*, 1924, 18, 314.

<sup>280</sup> Numerous synthetic resins have been suggested for this purpose; the index gives a complete list of those mentioned elsewhere in this book. For the application of phenolic resins, see H. Dreyfus, British P. 326,520, 1928; *Chem. Abs.*, 1930, 24, 4910. French P. 683,075, 1929; *Chem. Abs.*, 1930, 24, 4598. British P. 341,890, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 4997. French P. 681,507, 1929, to New G. and S. Processes Syndicate, Ltd.; *Chem. Abs.*, 1930, 24, 4369. C. H. Field and D. Haslett, British P. 321,178, 1928; *Chem. Abs.*, 1930, 24, 2567. A review on safety glass has been contributed by H. Schmidt, *Metalibörse*, 1932, 22, 1373; *Chem. Age (London)*, 1932, 27, 472.

<sup>281</sup> *Plastics*, 1934, 10, 131. French P. 673,668, 1928, to Soc. anon. des manufactures des glaces et produits chim. de Saint-Gobain, Chauny et Crey; *Chem. Abs.*, 1930, 24, 2568. Cf. the union of metal sheets with solutions of phenol-formaldehyde condensation products, French P. 644,333, 1927, to Aluminium-Walzwerke Singen, Lauber, Neher Co. G.m.b.H.; *Chem. Abs.*, 1929, 23, 1752.

<sup>282</sup> J. E. Alcock, British P. 319,873, 1928; *Chem. Abs.*, 1930, 24, 2568.

<sup>283</sup> B. Long, U. S. P. 1,668,853, May 8, 1928, to Soc. anon. des manufactures des glaces et produits chim. de Saint-Gobain, Chauny et Crey; *Chem. Abs.*, 1928, 22, 2248.

<sup>284</sup> British P. 345,758, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1932, 26, 574.

<sup>285</sup> L. C. F. Pechin, French P. 698,411, July 5, 1930; *Chem. Abs.*, 1931, 25, 3137. See also British P. 354,280, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1933, 27, 383.

<sup>286</sup> E. J. Sweetland, F. W. Manning and W. S. Hilpert, (U. S. P. 1,292,535, Jan. 28, 1919; *J.S.C.I.*, 1919, 38, 276A) used a similar product as an acid-resistant filter cloth.

<sup>287</sup> W. H. Moss, U. S. P. 1,860,687, May 31, 1932, to Celanese Corp. of Amer.; *Chem. Abs.*, 1932, 26, 2888. British P. 307,462, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs.* B, 1930, 205.

<sup>288</sup> H. O. Keay, U. S. P. 1,655,371, Jan. 3, 1928, to Laurentide Co., Ltd.; *Chem. Abs.*, 1928, 22, 1024. See also L. H. Bakeland, U. S. P. 1,019,407, Mar. 5, 1912, to Gen. Bakelite Co.; *Chem. Abs.*, 1912, 6, 1377. Cf. the preparation of waterproof sandpaper, R. P. Carlton, U. S. P. 1,775,831, Sept. 16, 1930, to Minnesota Mining & Mfg. Co.; *Chem. Abs.*, 1930, 24, 5452. British P. 267,510, 1926; *Chem. Abs.*, 1928, 22, 1244.



and furfural to unite pulp-grinding stones. Porcelain insulators have been joined together by similar compositions.<sup>290</sup> Merritt<sup>290</sup> spread a dry powder of phenolic resin over a sheet of mineral board, placed a veneer on top and united the sheets by subjecting to heat and pressure.

### VARIOUS IMPREGNATED BODIES

Phenol-aldehyde condensation products are used as impregnants for wood, concrete, asbestos millboard and electrical coils. The products differ from those described under laminated materials in that the former are in nearly their final shape before impregnation. However, the resin serves in approximately the same ways, i.e., as a binder and to increase the resistance to water, chemicals and the weather. As with laminated materials and molding compositions, it has been proposed to prepare the impregnant *in situ*. Aylsworth<sup>291</sup> saturated the object to be indurated with a solution of hexamethylenetetramine, dried and then treated at 76-99°C. with a solution of a fusible phenolic resin. The body was finally heated to transform the impregnant into the infusible form. Another method of preparing the resin *in situ* employs aldehyde-ammonia in place of hexamethylenetetramine.<sup>292</sup> The use of furfural with a condensation product which liberates ammonia during transformation to the infusible state will prevent the formation of bubbles.<sup>293</sup>

Studies on the properties of impregnated wood have been made by Schmidt,<sup>294</sup> Brajnikoff<sup>295</sup> and Klinov.<sup>296</sup> It was noted that the tensile and compressive strengths parallel to the grain could be doubled and the amount of water absorbed after a month's soaking was decreased by about 95 per cent.<sup>297</sup> The natural color of the wood was changed very little and the material could be easily worked and machined. Beech wood was made practically impervious to steam and had its resistance toward various acids (80 per cent acetic, 36.9 per cent hydrochloric and concentrated phosphoric), 5 per cent sodium hydroxide solution and the halogens greatly improved. Methyl and ethyl alcohols, acetone, ether, benzene and benzine had no effect at room temperature whereas chloroform and hot (90°C.) transformer oil had a swelling action. Concentrated sulphuric and nitric acids and cold 20 per cent caustic potash solution were the only reagents which attacked the material seriously. Such impregnated wood has been suggested for flooring, furniture,<sup>298</sup> machine bearings,<sup>299</sup> battery-wells<sup>300</sup> and golf-club heads.<sup>301</sup>

Brown<sup>302</sup> molded electrical insulators from portland cement and treated them

<sup>290</sup> British P. 361,852, 1930, to Porzellanfabrik Ph. Rosenthal & Co., A.-G.; *Chem. Abs.*, 1933, 27, 1129. Hemp is the filler used in British P. 362,233, 1931, to Hermadorf-Schomburg-Isolatoren G.m.b.H.; *Chem. Abs.*, 1933, 27, 1129. Cf. German P. 512,804, 1928, to Elektrizitäts A.-G. vorm. W. Lahmeyer & Co.; *Chem. Abs.*, 1931, 25, 1304.

<sup>291</sup> E. H. Merritt, U. S. P. 1,978,807, Oct. 30, 1934, to Laminating Patents Corp.; *Chem. Abs.*, 1935, 29, 257.

<sup>292</sup> J. W. Aylsworth, U. S. P. 1,111,286, Sept. 22, 1914, to Condensite Co. of Amer.; *Chem. Abs.*, 1914, 8, 3624. See also U. S. P. 1,047,484, Dec. 17, 1912; *Chem. Abs.*, 1913, 7, 712.

<sup>293</sup> A. Kanzok, Swiss P. 141,109, Jan. 2, 1928; *Chem. Abs.*, 1931, 25, 2311.

<sup>294</sup> British P. 322,789, 1928, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 2905. French P. 664,869, 1928; *Chem. Abs.*, 1930, 24, 942.

<sup>295</sup> H. Schmidt, *Kunststoffe*, 1931, 21, 251; *Chem. Abs.*, 1932, 26, 823.

<sup>296</sup> B. J. Brajnikoff, *Ind. Chemist*, 1930, 6, 502; 1931, 7, 32, 53, 115, 157; *Chem. Abs.*, 1932, 26, 284.

<sup>297</sup> I. Klinov, *Khimistron*, 1933, 5, 2310; *Chem. Abs.*, 1933, 27, 5219.

<sup>298</sup> J. J. Kessler (U. S. P. 1,638,342, Aug. 9, 1927; *Chem. Abs.*, 1927, 21, 3432) proposed to further increase the water-resistance of impregnated objects with a coat of oil varnish.

<sup>299</sup> J. W. Aylsworth, U. S. P. 1,111,286, Sept. 22, 1914, to Condensite Co. of Amer.; *Chem. Abs.*, 1914, 8, 3624.

<sup>300</sup> British P. 284,654 and 286,305, 1927, to Manufacture de machines auxiliares pour l'electricite et l'industrie; *Chem. Abs.*, 1928, 22, 4739; 1929, 23, 248.

<sup>301</sup> F. L. Dyer, U. S. P. 994,067, May 30, 1911, to T. A. Edison, Inc.; *Chem. Abs.*, 1911, 5, 2470.

<sup>302</sup> N. A. Rose, U. S. P. 1,583,617, June 15, 1926.

<sup>303</sup> A. H. Brown, British P. 259,505, 1925, to Siluminite Insulator Co., Ltd.; *Chem. Abs.*, 1927, 21, 3405. See also A. Zivy, British P. 381,694, 1931; *Brit. Chem. Abs. B.*, 1933, 81. Cf. the inclusion of resin in the original molding composition, A. H. Brown, British P. 260,653, 1925, to Siluminite Insulator Co., Ltd.; *Chem. Abs.*, 1927, 21, 3405.

with a liquid phenolic resin at 60-80°C. The latter was then hardened at 100-130°C. The addition of a phenol-aldehyde condensation product in alkaline solution to the mixing water of cement has also been suggested.<sup>303</sup> Silicate grinding wheels may be similarly strengthened by indurating with phenolic resins.<sup>304</sup> Howes<sup>305</sup> investigated the effect of continued heating on the electrical properties of field coils<sup>306</sup> impregnated with a phenol-formaldehyde condensation product. A continuous increase in resistance and decrease in power factor were noted. Except for mechanical deterioration, which was considerable at 150°C., the coils showed signs of lasting indefinitely.

Although asbestos sheets saturated with phenolic resins have been proposed as shields for the dies used in molding electrical insulators<sup>307</sup> and as spacers in heat-insulations,<sup>308</sup> a more important use has been as clutch facings and brake bands. According to Novak,<sup>309</sup> impregnation has the advantage over molding in that curved molds are not required since the treated strip can be shaped on a roll before hardening the resin. It has been suggested to use rosin along with the phenolic binder for the purpose of increasing friction. Thus, Fisher<sup>310</sup> used an alcoholic solution of soluble condensation product and rosin (not more than 10 per cent of the weight of the asbestos) to saturate asbestos rings which were then dried and heated to 150-200°C. Since both rosin and certain of the phenol-formaldehyde resins will dissolve in alkali, Novak<sup>311</sup> has employed alkaline solutions as impregnants. The saturated material was dipped into a bath of 10 per cent sulphuric acid to precipitate the binder and rosin. Castor oil has also been included to act both as a solvent during the impregnation and as an agent for increasing flexibility.<sup>312</sup> When the solvent used is a drying oil, it serves as an additional binder.<sup>313</sup> Frood<sup>314</sup> formed friction-elements, stair-treads, and soles and heels for shoes from fibrous materials held together with a mixture of rubber and dammar gum. He reports that a phenol-aldehyde condensation product can be included if desired.<sup>315</sup> Other asbestos objects have been made which were impregnated with both asphalt and phenolic resins. The material could be saturated first with the asphalt<sup>316</sup> or

<sup>303</sup> D. Trenniet, German P. 524,796 and 537,505, 1930, to Kasp. Winkler & Co. G.m.b.H., *Chem. Abs.*, 1931, 25, 4329; 1932, 26, 1412.

<sup>304</sup> C. R. King, U. S. P. 1,208,330, Dec. 12, 1916, to Norton Co.; *J.S.C.I.*, 1917, 36, 85. Cf. the addition of Bakelite to a boron-nitride insulator bound with silicic acid, S. Just, British P. 357,510, 1,30; *Brit. Chem. Abs. B.*, 1931, 1104.

<sup>305</sup> D. E. Howes, *Trans. Am. Electrochem. Soc.*, 1923, 44, 57; *Chem. Abs.*, 1923, 17, 3614.

<sup>306</sup> For the impregnation of such coils see L. H. Baekeland, U. S. P. 1,213,144 and 1,213,726, Jan. 23, 1917, to General Bakelite Co.; *Chem. Abs.*, 1917, 11, 878, 919. See also J. J. Kessler, U. S. P. 1,591,534, July 8, 1926; *Chem. Abs.*, 1926, 20, 3242. R. P. Jackson, U. S. P. 1,323,284, Dec. 2, 1919; *Chem. Abs.*, 1920, 14, 359. Allgem. Elektrizitäts-Ges., British P. 379,918, 1932, to International General Elec. Co., Inc.; *Chem. Abs.*, 1933, 27, 3543. Cf. the manufacture of magnetic structures from strips of nickel-iron alloy spaced apart with a phenol condensation product, British P. 241,384, 1924, to Western Electric Co., Ltd.; *Brit. Chem. Abs. B.*, 1926, 61.

<sup>307</sup> J. A. Crabtree and J. R. Dolphin, British P. 306,247, 1928; *Chem. Abs.*, 1929, 23, 4963.

<sup>308</sup> S. H. H. Barriatt, British P. 222,719, 1923, to Bell's United Asbestos Co., Ltd.; *Chem. Abs.*, 1925, 19, 1171.

<sup>309</sup> I. J. Novak, U. S. P. 1,561,740, Nov. 17, 1925, to Raybestos Co.; *Chem. Abs.*, 1926, 20, 268. See also T. M. Russell, U. S. P. 1,755,391, Dec. 16, 1930, to Russell Mfg. Co.; *Chem. Abs.*, 1931, 25, 567. Cf. British P. 284,268 and 284,269, 1927, to Kuehbach'sche Werke Kirchbuch & Co.; *Chem. Abs.*, 1928, 22, 4740.

<sup>310</sup> W. C. Fisher, U. S. P. 1,436,158, Nov. 21, 1922, to Russell Mfg. Co.

<sup>311</sup> I. J. Novak, U. S. P. 1,519,322, Dec. 16, 1924, and 1,672,538, June 5, 1928, to Raybestos Co.; *Chem. Abs.*, 1925, 19, 565; 1928, 22, 2645.

<sup>312</sup> W. Achemeyer, U. S. P. 1,599,627, Sept. 14, 1926, to Russell Mfg. Co.; *Chem. Abs.*, 1926, 20, 3544. See also I. G. Novak, U. S. P. 1,766,934, June 24, 1930, to Raybestos-Manhattan, Inc.; *Chem. Abs.*, 1930, 24, 4365.

<sup>313</sup> I. J. Novak, U. S. P. 1,766,932, June 24, 1930, to Raybestos-Manhattan, Inc.; *Chem. Abs.*, 1930, 24, 4365. See also U. S. P. 1,790,944, Feb. 3, 1931; *Chem. Abs.*, 1931, 25, 1646. British P. 357,420, 1930; *Chem. Abs.*, 1932, 26, 4144. French P. 710,213, 1930; *Chem. Abs.*, 1932, 26, 1080. R. E. Spokes, U. S. P. 1,961,177, June 5, 1934, to American Brakeblok Corp.; *Chem. Abs.*, 1934, 28, 4850.

<sup>314</sup> H. Frood, British P. 176,404, 1920, and 191,089, 1921; *Chem. Abs.*, 1922, 16, 2304; 1923, 17, 2941.

<sup>315</sup> Cf. the preparation of shoe lasts from paper pulp impregnated with a "carboloid" compound, E. I. Aiken, U. S. P. 1,650,232, Aug. 18, 1925; *Chem. Abs.*, 1925, 19, 3578.

<sup>316</sup> R. C. Neville, French P. 701,389, 1930; *Chem. Abs.*, 1931, 25, 4097. British P. 336,731, 1929; *Chem. Abs.*, 1931, 25, 1926.

with the synthetic binder<sup>317</sup> or the latter could be formed *in situ* (phenol included with the bituminous material and then treated with formaldehyde after the impregnation).<sup>318</sup>

### DECORATION OF MOLDED AND LAMINATED OBJECTS

A number of workers have attempted to prepare more attractive objects by various methods of decorating. One of the simplest is to mix molding powders of different colors. These will flow in the mold, resulting in a grained or mottled appearance.<sup>319</sup> Frederick<sup>320</sup> suggested that a similar effect could be obtained in laminated material by using differently colored sheets. Embossed designs have also been applied to partially cured articles and then hardened in place.<sup>321</sup> Carter<sup>322</sup>



FIG. 82.—  
Piling Sheets of Paper  
Impregnated with Phenolic Resin.

Courtesy Bakelite Corp.

proposed to form laminated sheets having a surface layer carrying a design. This was impregnated with a clear binder and backed with an opaque coating of titanium oxide or zinc sulphide. Carbon transfers and decalcomanias have been similarly applied to the surfaces of molded articles and then covered with a liquid resin which was finally hardened in place.<sup>323</sup> A thin imitation wood veneer was made by McIntosh<sup>324</sup> from an impregnated sheet of paper which had been laid on a thick body of fibrous material. After the binder had set, the sheet was removed with an adhering portion of fibrous material.

<sup>317</sup> L. Kirschbraun, U. S. P. 1,498,386, June 17, 1924, to Raybestos Co.; *Chem. Abs.*, 1924, 19, 30. British P. 185,809, 1921; *J.S.C.I.*, 1922, 41, 867A.

<sup>318</sup> L. Kirschbraun, U. S. P. 1,466,907, Sept. 4, 1923; *Chem. Abs.*, 1923, 17, 3759.

<sup>319</sup> F. P. Brock, U. S. P. 1,747,574, Feb. 18, 1930, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 1711. British P. 336,264, 1929; *Chem. Abs.*, 1931, 25, 2012. H. N. Copeland, U. S. P. 1,593,525, July 20, 1926, and 1,735,674, Nov. 12, 1930, to Kurz-Kasch Co.; *Chem. Abs.*, 1926, 20, 3216; 1930, 24, 699.

<sup>320</sup> L. T. Frederick, U. S. P. 1,284,644, Nov. 12, 1918, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1919, 13, 170.

<sup>321</sup> H. P. Mills, U. S. P. 1,742,516, Jan. 7, 1930, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 1189. British P. 336,265, 1929; *Chem. Abs.*, 1931, 25, 2012. See also J. W. Aylsworth, U. S. P. 1,694,828, Apr. 28, 1914, to Condensite Co. of Amer.; *Chem. Abs.*, 1914, 8, 2268.

<sup>322</sup> W. W. Carter, Jr., U. S. P. 1,956,314, April 24, 1934, to Formica Insulation Co.; *Chem. Abs.*, 1934, 28, 4202. See also A. V. Keller, British P. 333,763, 1929; *Chem. Abs.*, 1931, 25, 610. C. M. Hargrave, U. S. P. 1,634,830, July 5, 1927; *Chem. Abs.*, 1927, 21, 2993. G. H. Mains, U. S. P. 1,808,984, June 16, 1931, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1931, 25, 4674.

<sup>323</sup> L. C. Byck and G. L. Peakes, U. S. P. 1,815,234, July 21, 1931, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 5585. *Reissue* 19,549, Apr. 30, 1935.

<sup>324</sup> J. McIntosh, U. S. P. 1,661,901, March 6, 1928, to Diamond State Fibre Co.; *Chem. Abs.*, 1928, 22, 1487.

Several methods of coating molded articles with metals have been suggested. Eaton<sup>325</sup> sprinkled finely divided copper or aluminum over the surface of the mold. Powdered carbon has been added to a molding composition to make it electrically conductive. A coating of metal could then be electrodeposited on the finished molding.<sup>326</sup> Other processes form a thin film of an easily reduced metal salt on the surface. On reduction, the layer formed is conductive, permitting subsequent electroplating with additional metal.<sup>327</sup>

Petrov<sup>328</sup> reports that articles obtained from phenol-aldehyde condensation products can be colored or rendered resistant to attack by the atmosphere through immersing them in solutions of dyes and protective agents, e.g., quaiol, aminophenols, tannin, shellac and cellulose ethers. The dyes are fixed by treatment with dichromate solution. Another suggestion was to treat the articles with aqueous solutions of phenols or sulphonic acids before placing in the coloring bath.<sup>329</sup> The manufacture of artificial pearls has been attempted by Paiseau<sup>330</sup> through the use of shiny particles (obtained from fish scales or from swimming bladders) as fillers. Similar results are also stated to be obtained by using barium thiosulphate and various precipitates, e.g., fatty acids from soaps, uric acid from sodium urate, tin sulphate and cadmium iodide.<sup>331</sup> According to Parkert,<sup>332</sup> a more successful result is obtained if the decorative material is present in a layer and is covered with a number of thin coatings of celluloid and phenolic resin.

#### MISCELLANEOUS APPLICATIONS

The phenol-aldehyde condensation products are compatible with quite a number of other binders. The mixtures in some cases have found application since the properties differ from those of either ingredient.<sup>333</sup> Moss and Crutchfield<sup>334</sup> proposed to use an adhesive containing cellulose acetate and a urea-phenol-formaldehyde resin in making safety glass. According to Gardner,<sup>335</sup> an electrically insulating thread may be made by extruding an acetone solution of 5 g. of phenol-formaldehyde resin, 5 g. of shellac and 100 g. of cellulose acetate containing 10 g. of finely divided mica. If desired, viscose<sup>336</sup> can be employed in place of the ester. Films and filaments have also been formed from colloidal suspensions of phenol-formaldehyde condensation products containing dissolved alkyl celluloses.<sup>337</sup>

Rubber has been included in a phenol-aldehyde adhesive to join elastic sheets to

<sup>325</sup> J. Eaton, British P. 301,432, 1927, to Brit. Thomson-Houston Co., Ltd., *Chem. Abs.*, 1929, 23, 4070.

<sup>326</sup> L. J. Gloster, British P. 363,432, 1930, to J. Gloster, Inc., *Chem. Abs.*, 1933, 27, 1579.

<sup>327</sup> A. I. Gates-Warren, British P. 280,651 and 284,786, 1926, to Precious Metal Industries, Ltd.; *Chem. Abs.*, 1928, 22, 3129, 4740. A. I. Gates-Warren and E. L. Gates-Warren, British P. 299,903, 1927, to Precious Metal Industries, Ltd.; *Chem. Abs.*, 1929, 23, 3548.

<sup>328</sup> G. Petrov, U. S. P. 1,865,586, July 8, 1932; *Chem. Abs.*, 1932, 26, 4425. British P. 292,636, 1927; *Brit. Chem. Abs. B*, 1928, 648.

<sup>329</sup> G. Petrov, British P. 292,637, 1927, addn. to 292,636, 1927; *Brit. Chem. Abs. B*, 1928, 648. French P. 33,532, 1927, addn. to 629,251; *Chem. Abs.*, 1929, 23, 2540.

<sup>330</sup> J. Paiseau, U. S. P. 1,525,317, Feb. 3, 1925; *Chem. Abs.*, 1925, 19, 1036. British P. 183,774, 1921, and 229,585, 1924; *J.S.C.I.*, 1923, 42, 55A; 1925, 44, 316B.

<sup>331</sup> J. Paiseau, U. S. P. 1,546,309, July 14, 1925; *Chem. Abs.*, 1925, 19, 2867. J. Paiseau and R. Warcollier, British P. 222,881, 1924; *J.S.C.I.*, 1925, 44, 957B.

<sup>332</sup> O. Parkert, *Kunststoffe*, 1925, 15, 98.

<sup>333</sup> In Chapter 20, there is a further account of a number of related modified phenol-formaldehyde resins.

<sup>334</sup> W. H. Moss and K. H. Crutchfield, Canadian P. 323,574, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 4432. See also W. H. Moss, Canadian P. 317,919, 1931, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 1409. British P. 347,445 and 365,094, 1930, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B*, 1931, 687; 1932, 357.

<sup>335</sup> H. A. Gardner, U. S. P. 1,730,417, Oct. 8, 1929; *Chem. Abs.*, 1929, 23, 5520. See also W. Dreyfus, French P. 39,028, 1930, addn. to 702,174, 1930; *Chem. Abs.*, 1932, 26, 1784.

<sup>336</sup> A modified viscose silk had been previously made by E. Bronnert, U. S. P. 1,374,718, April 12, 1921; *Chem. Abs.*, 1921, 15, 2730.

<sup>337</sup> G. Balle and K. Sponzel, German P. 827,197, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4708. British P. 308,284, 1927; *Chem. Abs.*, 1930, 24, 239.

metal.<sup>338</sup> Trist<sup>339</sup> reports that a packing composed of textile material in a matrix of rubber can be treated so that it is resistant to oil, acid and alkali by immersing it in a mixture of solvents, one constituent of which softens the rubber and the other is a solvent for the resistant substance. Shellac and bitumen are used to give oil- and acid-resisting packings respectively. Synthetic resins of the phenol class can also be employed. The addition of a phenolic condensation product to a rubber-bound abrasive wheel is said to render the product less affected by heat changes.<sup>340</sup> Benjamin<sup>341</sup> states that a substitute for leather can be made from the reaction product of cresol and formaldehyde. He proposed the following composition: rubber (23.8 per cent), synthetic resin (2.6 per cent), sulphur (1.1 per cent), asbestos (6.1 per cent), mica (42 per cent), cotton shoddy (17.5 per cent), lamp-black (1.7 per cent) and litharge (5.2 per cent). Separators for electrical accumulators have been produced from diatomaceous earth held together with a binder consisting of rubber and a phenolic resin.<sup>342</sup>

Coleman and Groten<sup>343</sup> report that compositions which contain mixtures of drying oils, asphaltic material, copal and rapid-hardening plastics (phenol-formaldehyde) as binders can be removed from the mold after less time than can the usual types of hot-molding powder.<sup>344</sup> The articles are baked at a gradually rising temperature for 8-40 hours to complete the hardening. The products have a good polish and adequate strength. Sandpaper has been prepared using linseed oil to waterproof the backing and also as a component of the adhesive.<sup>345</sup> Laminated stock made from sheets of paper impregnated alternately with drying oils and phenolic resins are said to have considerable mechanical strength and elasticity.<sup>346</sup>

The condensation products which are obtained from the action of formaldehyde on phenols precipitate albuminoids, e.g., glue and gelatin, from their solutions. However, Arnot<sup>347</sup> reports that, if the glue is partially hydrolyzed before adding the condensation product, no coagulation takes place.

For example, 500 parts of 40 per cent formaldehyde were run into 1000 parts of dark cresylic acid (97 per cent) and then 20 parts of finely powdered bleaching powder were added. The temperature was held at 90°C. for about 30 minutes after which the mixture is allowed to stand for an hour. The oily layer was run while still hot into liquid glue. The latter was prepared by heating 1200 parts of ground hideglue, 24 parts of sodium bicarbonate and 2000 parts of water in an autoclave at 130°C. for 2.5-3 hours. The adhesive formed by mixing the two liquids is stated to be applicable

<sup>338</sup> O. A. Thompson, U. S. P. 1,931,309, Oct. 17, 1933, to B. F. Goodrich Co., *Chem. Abs.*, 1934, 28, 374. French P. 723,088, 1931, *Chem. Abs.*, 1932, 26, 4207.

<sup>339</sup> A. R. Trist, British P. 405,987, 1934, *Chem. Abs.*, 1934, 28, 4850.

<sup>340</sup> D. E. Webster, U. S. P. 1,655,396, Jan. 3, 1928, *Chem. Abs.*, 1928, 22, 1024. See also British P. 403,698, 1933, to Carborundum Co., Ltd.; *Chem. Abs.*, 1934, 28, 3850. R. C. Benner and G. H. Porter (U. S. P. 1,825,771, Oct. 6, 1931, to Carborundum Co.; *Chem. Abs.*, 1932, 26, 574) have used a number of rubber derivatives with phenol resins in abrasive wheels. Cf. the addition of phenol-formaldehyde to a brake block from asbestos fiber held together with rubber. D. Repony, U. S. P. 1,930,227, Nov. 13, 1934, to Raybestos-Manhattan, Inc.; *Chem. Abs.*, 1935, 29, 252.

<sup>341</sup> E. O. Benjamin, U. S. P. 1,493,062, May 6, 1924, *Chem. Abs.*, 1924, 18, 2088.

<sup>342</sup> British P. 377,257, 1931, to Chloride Electrical Storage Co., Ltd.; *Brit. Chem. Abs.*, 1932, 944.

<sup>343</sup> R. E. Coleman and F. J. Groten, U. S. P. 1,808,529, June 2, 1931, to Monowatt Elec. Corp.; *Chem. Abs.*, 1931, 25, 4370. See also J. M. de Bell, British P. 345,489, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1932, 26, 2073. French P. 691,896, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 1400. Cf. German P. 561,656, 1929, to Bakelite G.m.b.H.; *Chem. Abs.*, 1932, 27, 1221.

<sup>344</sup> A similar mixture of stable and unstable thermoplastic bodies has been used as a box toe stiffener. L. P. Mellerio and W. J. Lund, U. S. P. 1,846,346, Feb. 23, 1932, to United Shoe Machinery Corp.; *Chem. Abs.*, 1932, 26, 2562.

<sup>345</sup> C. A. Klein and R. S. Brown, U. S. P. 1,687,453, Oct. 9, 1928; *Chem. Abs.*, 1928, 22, 4751. Cf. the flexible and waterproof sandpaper made by F. G. Okie (British P. 226,803, 1923, *Chem. Abs.*, 1925, 19, 2114) using linseed oil as binder and phenolic resins in a sizing.

<sup>346</sup> E. Elbel and F. Seebach, German P. 589,071, 1933, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 1427. Cf. the manufacture of loom pickers from a similar material in which the alternate layers consist of fabric impregnated with raw rubber. Allgem. Elektrizitäts-Ges., British P. 352,522, 1929, to International General Elec. Co.; *Chem. Abs.*, 1933, 27, 611.

<sup>347</sup> R. Arnot, U. S. P. 1,771,553, July 29, 1930; *Chem. Abs.*, 1930, 24, 4597. British P. 225,953, 1923; *Chem. Abs.*, 1925, 19, 1619. Cf. British P. 333,194, 1929; *Chem. Abs.*, 1931, 25, 566.

to the uniting of wood veneers. At a pressure of 300 pounds per square inch and a temperature of 110-120°C., the gluing was effected in 8-10 minutes.<sup>540</sup>

An adhesive of greater elasticity was obtained by adding rubber or factice<sup>541</sup> to the cresol before condensation. Impermeable plastic masses are said to result when dried blood is incorporated with phenol before or after the condensing with formaldehyde.<sup>542</sup> A suggested leather substitute consists of leather scrap bound together by a phenol-formaldehyde condensation product mixed with albumin or keratinous substances.<sup>543</sup> Jeschke<sup>544</sup> heated glue with glycerol and then added a phenolic resin and continued heating until a tough viscous mass resulted. This was proposed as a binder in linoleum.<sup>545</sup>

Shellac and Manila copal have been included in plastic compositions,<sup>546</sup> cements<sup>547</sup> and impregnants<sup>548</sup> prepared from phenol-formaldehyde condensation products. In each case, the toughness of the material was said to be increased. Field and Haslett<sup>549</sup> mixed equal parts of a solution of Canada balsam in xylene and a solution of glycerol-phenol-formaldehyde resin in 40 per cent aqueous alcohol. Both liquids were of the consistency of syrup. The mixture was suggested as an adhesive in making safety glass.

A composition containing abrasive grains, phenols, aldehydes, hardening agent and an alkyd resin produced *in situ* has been used by Novotny<sup>550</sup> in the production of grinding wheels. Layers of fabric impregnated with glycerol-phthalic-anhydride-type resins have been bonded into laminated sheets with phenolic condensation products.<sup>551</sup> Such material is stated to be applicable in making machine parts which are required to resist shock. The use of small proportions of chloronaphthalene waxes as plasticizers for the phenol type of resins has already been mentioned. Aylsworth employed larger proportions in producing fireproof roofing<sup>552</sup> and furniture polish.<sup>553</sup> The latter consisted of cresol-formaldehyde condensation product (40-55 parts), chloronaphthalene wax (75 parts), acetylene tetrachloride (55-65 parts) and benzene (80-120 parts). A bearing for high-speed machinery has been made from sericite schist and pulverized lead held together with wax and a phenolic binder.<sup>554</sup>

Since impregnations with solutions usually possess a more or less porous structure after the solvent has evaporated, it has been suggested that the pores be par-

<sup>540</sup> A similar product has been employed in the manufacture of sandpaper. C. Klungspor, U. S. P. 1,833,715, Nov. 24, 1931; *Chem. Abs.*, 1932, 26, 1088. British P. 293,232 and 302,430, 1927; *Chem. Abs.*, 1929, 23, 1524, 4316.

<sup>541</sup> For a description of factice, see Chapter 60.

<sup>542</sup> German P. 466,053, 1926, to Pfennig-Schumacher-Werke G.m.b.H.; *Chem. Abs.*, 1929, 23, 1729. See also L. E. Barringer, British P. 345,390, 1930, to Brit. Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B. 1931, 598. Cf. the inclusion of casein. K. I. Tarasov, Russian Applications 24, 198 and 29,211, 1928, addns. to Patent 10,596; *Chem. Abs.*, 1931, 25, 2531.

<sup>543</sup> K. I. Tarasov, Russian P. 14,577 and 25,156, 1928; *Chem. Abs.*, 1933, 27, 1544.

<sup>544</sup> R. Jeschke, U. S. P. 1,421,086, June 27, 1922, to Phenoleum G.m.b.H.; *Chem. Abs.*, 1922, 16, 3004.

<sup>545</sup> Concerning the possibilities for employing synthetic resins in the linoleum industry, see A. B. Miller and F. D. Snell, *Ind. Eng. Chem.*, 1933, 25, 1807.

<sup>546</sup> French P. 653,007, 1928, to Worldecho, Ltd.; *Chem. Abs.*, 1929, 23, 3782. British P. 308,560, 1928; *Chem. Abs.*, 1930, 24, 253.

<sup>547</sup> F. A. Upper, U. S. P. 1,950,641, March 13, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 3552. E. R. Schmid, U. S. P. 1,626,700, May 3, 1927; *Chem. Abs.*, 1927, 21, 2174. L. E. Frost, U. S. P. 1,376,737, Mar. 16, 1920, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1920, 20, 1690.

<sup>548</sup> J. J. Kessler has used Manila gum, hexamethylenetetramine and phenol in both two-stage (U. S. P. 1,593,579, July 27, 1926; *Chem. Abs.*, 1926, 20, 3242) and one-stage impregnations (U. S. P. 1,612,894, Jan. 11, 1927; *Chem. Abs.*, 1927, 21, 806).

<sup>549</sup> C. H. Field and D. Haslett, British P. 321,189, 1928; *Chem. Abs.*, 1930, 24, 2568.

<sup>550</sup> E. E. Novotny, U. S. P. 1,907,083, May 2, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3577.

<sup>551</sup> British P. 200,636, 1928, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 4090. German P. 543,442, 1928; *Chem. Abs.*, 1932, 26, 2561. Cf. the electrical insulation formed by binding together asphalt-impregnated sheets. G. A. Burr, J. R. McClain and L. E. Frost, U. S. P. 1,448,386, Mar. 13, 1923, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1923, 17, 1853.

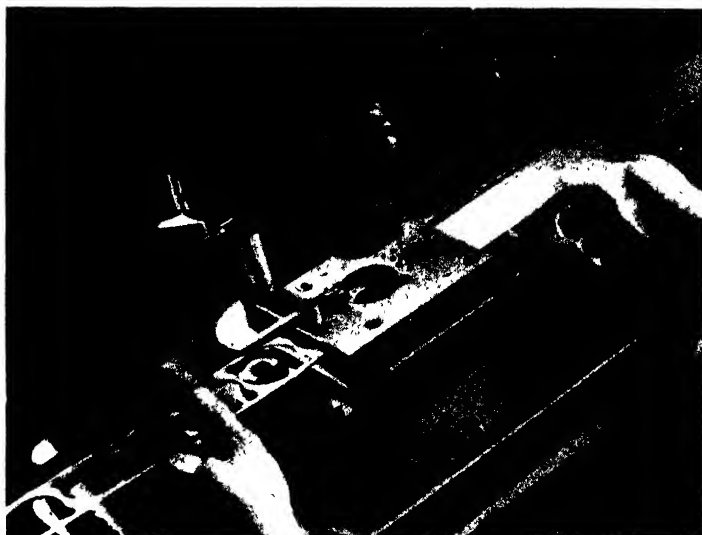
<sup>552</sup> J. W. Aylsworth, U. S. P. 1,077,113, Oct. 23, 1913, to Condensite Co. of Amer.; *Chem. Abs.*, 1914, 8, 231.

<sup>553</sup> J. W. Aylsworth, U. S. P. 1,090,440, Mar. 17, 1914; *Chem. Abs.*, 1914, 8, 1647.

<sup>554</sup> C. F. Noffsger, U. S. P. 1,963,184, Dec. 4, 1934; *Chem. Abs.*, 1935, 29, 533.

tially filled with sulphur previously.<sup>366</sup> In order to improve the molding properties, Nash<sup>364</sup> included in phenol resins 10 per cent of stearin pitch and 3 per cent of sulphur. The residues from the distillation of natural resins and tall oil<sup>365</sup> have been heated with sulphur and the vulcanized products incorporated with phenol-aldehyde binders.<sup>366</sup> A further industrial by-product with which phenol resins can be admixed is the gummy precipitate obtained by acidifying black liquor.<sup>367</sup>

For certain purposes objects with a porous structure are desired. One way in which these may be obtained is by using a filler which can be easily removed. Thus, dissolving out metal wires from a plate of phenol resin forms a series of orifices through which artificial silk may be extruded.<sup>368</sup> Porous bearings have been similarly made by the action of acid on a filler consisting of powdered metal.<sup>369</sup>



Courtesy Bakelite Corp.

FIG. 83.—Radio Insulation Being Punched from Laminated Stock.

In making abrasive wheels having definite predetermined interstices, the mold is first packed with lumps of sugar, naphthalene or cork which are later removed by dissolution or volatilization. In this case the openings provide fresh cutting-edges and cooling spaces.<sup>370</sup> Turkington<sup>371</sup> proposed to make noiseless gears by molding pieces of cloth having a reticulated structure. The latter was obtained by including water in the composition. The setting of the resin is accelerated

<sup>366</sup> F. A. Burningham, G. A. Richter, W. B. Van Arsdell and D. H. White, U. S. P. 1,396,021, Nov. 8, 1921, to Brown Co.; *Chem. Abs.*, 1922, 16, 647.

<sup>364</sup> C. A. Nash, U. S. P. 1,574,842, March 2, 1926; *Chem. Abs.*, 1926, 20, 1530.

<sup>365</sup> See Chapter 36.

<sup>366</sup> German P. 471,835, 1924, addn. to 455,551, to Sinit A.-G.; *Chem. Abs.*, 1929, 23, 2540.

<sup>367</sup> J. T. Collins, U. S. P. 1,716,623, June 11, 1929; *Chem. Abs.*, 1929, 23, 3782. T. M. Vinson, German P. 538,799, 1929; *Chem. Abs.*, 1932, 26, 2318. Black liquor is a by-product of the soda process for making wood pulp. See Chapter 36.

<sup>368</sup> E. Schülke and W. Elsner, British P. 161,526, 1921, to Sudenburger Maschinenfabr. & Eisengieserei A.-G.; *J.S.C.I.*, 1922, 41, 367A.

<sup>369</sup> J. Brincil, U. S. P. 1,771,615, July 29, 1930; *Chem. Abs.*, 1930, 24, 6048.

<sup>370</sup> T. Pohl and J. Schneider, U. S. P. 1,986,350, Jan. 8, 1935, to Deutsche Gold- & Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1935, 29, 1234. British P. 411,498, 1932; *Brit. Chem. Abs. B*, 1934, 718. Cf. the preparation of porous filter plates by the volatilization of paraffin. British P. 251,964, 1925, to Schumacher'sche Fabrik G.m.b.H.; *Chem. Abs.*, 1927, 21, 1531.

<sup>371</sup> V. H. Turkington, U. S. P. 1,958,452, May 15, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 4551. British P. 345,228, 1929; *Brit. Chem. Abs. B*, 1931, 687. See also the preparation of powdered phenolic resin by grinding the porous body obtained by letting a volatile solvent escape after hardening. J. W. Aylsworth, U. S. P. 1,092,512, Apr. 7, 1914, to Condensite Co. of Amer.; *Chem. Abs.*, 1914, 8, 1878.

(to avoid allowing the water to escape too soon) by the addition of a polymerizing-catalyst.<sup>373</sup> A further porous material consists of a fibrous mass in which there is not enough phenolic binder to completely fill the interstices.<sup>374</sup>

Fuller<sup>375</sup> stated that difficulty is sometimes encountered in determining by inspection whether molded articles have been heated to the right temperature. He suggested that a dye be included which would fade out when the material was hot enough. Malachite green and methyl violet were mentioned, since they are decomposed at about 180° and 220°C. respectively. The presence of 3-5 per cent of water in molding compositions was reported as preventing deformation due to further absorption.<sup>376</sup> Employment of a resin which will absorb not less than 18 per cent of water at 25°C. was also stated to give a laminated sheet with improved bending and splitting strength.<sup>376</sup>

Water-soluble salts of phenol-formaldehyde resins may be dissolved in less than the equivalent amount of alkali and then salted out of solution. When using an equivalent or greater quantity of alkali, the material cannot be salted out. The substances obtained are soluble in water, but when heated or treated with carbon dioxide the solutions are decomposed with partial precipitation of the condensation product. The products were said to find application in the textile industry.<sup>377</sup>

The suggestion has been made that free phenol (1 per cent) be left in molding compositions which were desired to have antiseptic properties.<sup>378</sup> Curley<sup>379</sup> recommended that a thin strip of phenolic resin be included in the frame of a tennis racket. Being tough and impervious to moisture, the insert helps to prevent warping. The difficulty which arises in attaching sheets of phenol-formaldehyde condensation products to metals has already been mentioned. This difference in thermal expansion was put to use by Aylsworth<sup>380</sup> who made molds for cylindrical metallic phonograph records from phenol resin. On warming the matrix, it expanded, freeing the record. Albrecht<sup>381</sup> proposed to fill teeth with a solution containing glycerol, a phenol condensation product and a condensing agent.

When heated to 800-900°C., phenolic resins are carbonized. The resulting material has been used as an absorbent charcoal<sup>382</sup> and in variable-resistance units of telephone transmitters.<sup>383</sup> In the latter case, a fusible condensation product was granulated and melted. The molten particles were allowed to assume a spherical shape and then hardened by slow heating to 270°C. previous to carbonizing. Mixtures of graphite and phenol-furfuraldehyde binders have been molded and then coked to form dynamo brushes.<sup>384</sup> If a small quantity of a rubber-vulcanization accelerator is included, the molded brush is said to be harder and more durable.<sup>385</sup> A similar procedure applies a layer of synthetic resin filled with colloidal charcoal to a ceramic carrier. After carbonization, the product was used in potentiometers.<sup>386</sup>

<sup>373</sup> British P. 379,675, 1932, addn. to 345,223, 1929, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 4106.

<sup>374</sup> British P. 419,629, 1933, to International Latex Processes, Ltd.; *Brit. Chem. Abs. B*, 1935, 98.

<sup>375</sup> C. T. Fuller, U. S. P. 1,580,346, Nov. 3, 1925, to General Elec. Co.; *Chem. Abs.*, 1926, 20, 267.

<sup>376</sup> French P. 691,295, 1930, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 1048.

<sup>377</sup> British P. 417,011, 1933, to Dynamit-A.-G. vorm. A. Nobel & Co.; *Brit. Chem. Abs. B*, 1934, 1071.

<sup>378</sup> French P. 764,240, 1934; *Chem. Abs.*, 1934, 28, 5612.

<sup>379</sup> H. Bucherer, German P. 350,048, 1918; *J.S.C.I.*, 1922, 41, 728A.

<sup>380</sup> F. S. Clifford, British P. 331,157, 1929; *Chem. Abs.*, 1930, 24, 6042.

<sup>381</sup> J. J. Curley, U. S. P. 1,094,703, Apr. 28, 1914.

<sup>382</sup> J. W. Aylsworth, U. S. P. 1,060,577, May 6, 1913, to T. A. Edison, Inc.

<sup>383</sup> J. A. Albrecht, U. S. P. 1,205,957, Nov. 28, 1916; *J.S.C.I.*, 1917, 36, 91.

<sup>384</sup> L. Wallerstein, U. S. P. 1,442,372, Jan. 16, 1923; *Chem. Abs.*, 1923, 17, 1115.

<sup>385</sup> R. S. Howard, U. S. P. 1,828,046, Oct. 20, 1931, to Western Elec. Co.; *Chem. Abs.*, 1932, 26, 813.

<sup>386</sup> Western Elec. Co., Inc., British P. 329,652, 1929, to Standard Telephones & Cables, Ltd.; *Brit. Chem. Abs. B*, 1930, 851.

<sup>387</sup> H. M. Williams and A. L. Boegehold, U. S. P. 1,856,680, May 3, 1932, to Gen. Motors Res. Corp.; *Brit. Chem. Abs. B*, 1933, 273.

<sup>388</sup> N. R. Haas, U. S. P. 1,703,191, Feb. 26, 1929, to Delco-Remy Corp.; *Chem. Abs.*, 1929, 23, 2002.

See also U. S. P. 1,729,343, Sept. 24, 1929, and 1,804,052, May 5, 1931; *Chem. Abs.*, 1929, 23, 5285; *Brit. Chem. Abs. B*, 1931, 1145.

<sup>389</sup> British P. 409,740, 1934, to Steatit-Magnesia A.-G.; *Chem. Abs.*, 1934, 28, 6253.

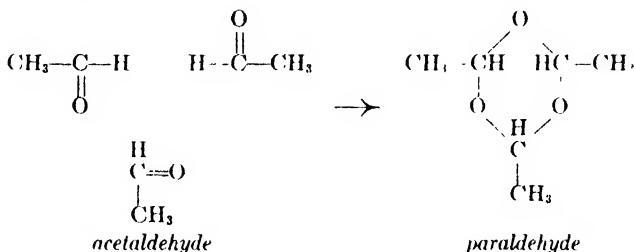


## Chapter 23

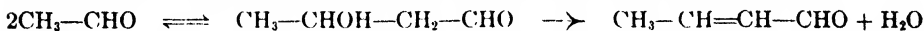
### Aldehyde Resins

Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) is a compound from which various kinds of resins may be made. By self- or auto-condensation, acetaldehyde undergoes two quite different series of reactions, one a carbon-oxygen-carbon, the other, a carbon-carbon union.

By treating acetaldehyde with a small amount of concentrated sulphuric acid, paraldehyde is formed.<sup>1</sup> This substance is readily decomposed by warming with dilute sulphuric acid.

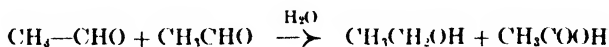


Mild alkaline reagents cause acetaldehyde to undergo a simultaneous intermolecular oxidation-reduction; the  $\alpha$ -hydrogen of one aldehyde reduces the carbonyl in the adjacent molecule with the result that a carbon-carbon bond is formed and the compound so obtained is known variously as  $\beta$ -hydroxybutyraldehyde, acetaldol or simply aldol. The reaction is likewise reversible. More easily, however, a loss of water occurs in acetaldol and crotonic aldehyde results.



Less strenuous acid conditions than used in the formation of paraldehyde also bring about aldolization.

Another type of simultaneous oxidation-reduction can take place, that is, where the aldehyde groupings undergo compensating changes, the so-called Cannizzaro reaction.



This reaction takes place in concentrated alkaline solution.

Consideration will first be given to the various means by which acetaldehyde may be resinified and subsequently to the conditions under which aldolization may take place. Acetaldehyde resins are obtained principally in alkaline solution. There are cases, however, where resinous substances have been formed under acid

<sup>1</sup> Metaldehyde is formed from acetaldehyde and acids at low temperatures, i.e., below  $0^\circ\text{C}$ . Other reagents for the transformation of acetaldehyde to metaldehyde include ammonium bromide, hydrazine hydrochloride, pyridine hydrobromide and perborate, halogenated pyridines, urea hydrochloride, diphenyl thiourea hydrobromide, the hydrohalides of alkylamines and hexamethylenetetramine, tetraethyl ammonium trichloride together with a strong inorganic acid. See British P. 235,867, 1924, to Elektrizitätswerk Lonsa; *Chem. Abs.*, 1926, 20, 917.

conditions and to a slight extent by the action of light and under the influence of atomic hydrogen and enzymes.

#### ALKALINE RESINIFICATION

Acetaldehyde and its derivatives, aldol and crotonaldehyde all undergo resinification in alkaline solution.\* The earliest observations of the resinification of acetaldehyde were made by Liebig<sup>3</sup> and Döbereiner.<sup>4</sup> Döbereiner noted that an alcoholic solution of potassium hydroxide when warmed with acetaldehyde furnished a yellowish or brown resin-like substance. Liebig observed that an aqueous solution of aldehyde, warmed with potassium hydroxide immediately became yellowish and turbid and quickly separated a reddish-brown substance which could be drawn out into long threads. He named the product aldehyde resin and noticed that it had a penetrating odor. According to Weidenbusch,<sup>5</sup> this odor is due to a volatile oil, which is oxidized by air to a resinous body. When dried at room temperature and subsequently over a water bath the resin was reported by Liebig to ignite spontaneously. Weidenbusch did not observe any such ignition.

Barium hydroxide may be used to bring about the condensation and the barium removed as carbonate by carbon dioxide. Filtration and concentration of the aqueous solution leaves a gummy syrup.<sup>6</sup> The resin can also be formed from alcoholic potash if air or some oxidizing agent is present.<sup>7</sup> Ekecrantz<sup>8</sup> prepared acetaldehyde resin as follows:

A mixture of acetaldehyde and alcohol is cooled to  $-20^{\circ}\text{C}.$ , and a 10 per cent alcoholic sodium hydroxide solution is added, the temperature of the mixture being kept below  $10^{\circ}\text{C}.$  The mixture is kept cold for some time, allowed to stand at room temperature for 24 hours and finally heated under a reflux condenser until the aldehydic odor has disappeared. The alcohol is removed by vacuum evaporation at approximately  $30^{\circ}\text{C}.$  A thick reddish-brown residue is obtained which when treated repeatedly with hot 5 per cent caustic soda solution sets to a brittle resin. Purification may be effected by dissolving in glacial acetic acid and precipitating with water. The acidic portion of the aldehyde resin which remains in solution with the caustic soda is obtained by neutralizing the alkali and extracting with ether. A yellowish-brown viscous residue is obtained.

Some elementary analyses of acetaldehyde resin by various early observers are given in Table 29.

TABLE 29.—Elementary Analyses of Acetaldehyde Resins.

	Liebig	Weidenbusch	Ekecrantz*
Carbon.....	73 34	76 40	70.07
Hydrogen.....	7.76	7 97	7.83
Oxygen.....	18.90	21 63	22 1

\* Ekecrantz ascribes the variation in the analytical results to a fluctuating water content.

<sup>2</sup> These three substances are to be treated separately, but it should be borne in mind that many investigators use all three interchangeably and many of the references to acetaldehyde refer or apply to aldol and crotonaldehyde as well.

<sup>3</sup> J. Liebig, *Ann.*, 1835, 14, 140. See L. Gmelin, "Handbook of Chemistry," translated by H. Watts for the Cavendish Society, London, 1866, 17, 456.

<sup>4</sup> J. W. Döbereiner, *Ann.*, 1835, 14, 140. Cf. Gmelin, *loc. cit.*

<sup>5</sup> Weidenbusch, *Ann.*, 1848, 66, 153; L. Gmelin, *loc. cit.*, 1866, 17, 456.

<sup>6</sup> B. Tollens, *Ber.*, 1884, 17, 660.

<sup>7</sup> Alcohol which contains pyridine and aldehyde, when burned in lamps, forms resinous substances, presumably from the condensation of aldehydes formed. See J. Dehnike and W. Kilp, *Z. spiritusind.*, 1926, 49, 280; *Chem. Abs.*, 1927, 21, 167. In Döbereiner's vinegar lamp, alcohol may oxidized to acetic acid in the presence of air. In a deficiency of air, aldehyde is formed; if this is absorbed by caustic potash, a yellow resin is obtained; J. S. Döbereiner, *Schweigg. Jour.*, 1831, 63, 223. See L. Gmelin, *loc. cit.*, 1835, 8, 207; also A. Mittasch and E. Theis, "Von Davy und Döbereiner bis Deacon," Verlag Chemie G.m.b.H., Berlin, 1932, 79.

<sup>8</sup> T. Ekecrantz, *Arkiv för Kemi*, 4, 27, 1; *Chem. Zentr.*, 1912, 2, 1193. See M. Bottler, "Kunstharsen" J. F. Lehmanns Verlag, München, 1919, 42.

By means of the varying solubilities in benzene, Ekecrantz was able to separate aldehyde resin into two components,  $\alpha$  and  $\beta$ ; the  $\alpha$ -resin is soluble in this solvent, the other very much less so. Both resins may be represented by the formula,  $C_{24}H_{36}O_6$  or  $[12(CH_2CHO) - 6H_2O]$ .

Hammarsten<sup>9</sup> allowed aqueous solutions of acetaldehyde to remain for 5-6 days at ordinary temperatures with an equal volume of 10 per cent aqueous potassium hydroxide solution. A red-colored resin was obtained by neutralizing the solution with acid. Further addition of concentrated hydrochloric acid to the filtrate caused the separation of a very pale straw-yellow resin which had a melting point of 120-130°C.; decomposition occurred above 200°C. Analyses revealed a molecular weight of 396-412. Hammarsten was uncertain whether the red resin was formed independently or through the yellow variety. An alkaline solution of the yellow resin did not become turbid when preserved. This suggests that the red resin is formed through a different series of reactions.

Some of the properties of acetaldehyde resin are given by Weidenbusch.<sup>10</sup> He stated that the resin is a bright orange-yellow powder becoming lighter in color on long drying at 100°C. It is soluble in ether and slightly soluble in water. Ekecrantz<sup>11</sup> noted that acetaldehyde resin is soluble in chloroform, alcohol and acetone, only partially soluble in benzene and ether, and insoluble in petroleum ether. At 105°C. the resin sinters and at 130-140°C. melts and intumescs.

The processes described by Liebig, Döbereiner and Ekecrantz remain to this day fundamental for the production of acetaldehyde resin. These resins, as such, have found little place in commerce and many efforts have been made to alter their properties in order that they might be used.

An appreciable quantity of aldehyde resin was obtained by Pauly and Feuerstein<sup>12</sup> by the following procedure: To 1.5 l. of 6 per cent acetaldehyde solution on the water bath at 70°C. were added 40 cc. of 5 per cent caustic potash solution with shaking. As the alkali disappeared, further portions were added, 5 cc. at a time, the total quantity amounting to 65 cc. The mixture was held for 6 hours at 66°C. and a yellowish-red oil subsequently isolated by cooling, neutralizing with acetic acid and salting out with sodium chloride. The product was repeatedly extracted with benzene and the solution in the latter dried with calcium chloride; vacuum distillation yielded 26 g. of resin. In the distillate were detected two unsaturated aldehydes with the formulas,  $C_8H_{12}O_2$  and  $C_{10}H_{14}O_2$ .

According to Herrmann and Deutsch,<sup>13</sup> acetaldehyde resin is acted upon by water to form a muddy material. To eliminate this tendency, 100 parts of acetaldehyde condensation product (produced in the presence of caustic soda) were ground with 200 parts of a 3 per cent aqueous solution of acetic acid. The swollen resin particles were filtered from the resulting suspension and remelted, yielding a body which was no longer acted upon by water. Similar results may be obtained also by dissolving the resinous products in alcohol or acetone and precipitating the dissolved resins from the solution with water.

The degree of hardness of acetaldehyde resins increases, according to Herrmann and Deutsch,<sup>14</sup> with the duration and intensity of treatment with alkali. In a process given by them, 500 parts of acetaldehyde are slowly introduced into a container with 300 parts of 20 per cent sodium hydroxide solution, the latter being cooled and vigorously stirred. The fluid products which are first formed soon become viscous and finally solid upon continued action of the alkali. Depend-

<sup>9</sup> H. Hammarsten, *Ann.*, 1920, 421, 293; *J.C.S.*, 1920, 118 (1), 818.

<sup>10</sup> Weidenbusch, *loc. cit.*

<sup>11</sup> T. Ekecrantz, *loc. cit.*

<sup>12</sup> H. Pauly and K. Feuerstein, *Ber.*, 1929, 62, 369.

<sup>13</sup> W. O. Herrmann and H. Deutsch, *U. S. P.* 1,596,971, Aug. 24, 1926; *Chem. Abs.*, 1926, 20, 3354.

<sup>14</sup> W. O. Herrmann and H. Deutsch, *U. S. P.* 1,767,759, June 24, 1930, to Consort. für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1930, 24, 4409. See German P. 379,332, 1920; *J.S.C.I.*, 1924, 43, 141B.

ing on the duration and manner of treatment, the resins are transparent or nearly opaque and may vary from a light yellow to a dark reddish brown. The melting point of the resins may be raised to above 200°C. by continued action of alkali, yielding materials soluble in alcohol, acetone, anhydrous acetic acid, linseed oil and turpentine oil. Solutions of the resins may be used for varnishing and polishing purposes and are reported useful for first-coating and impregnation of wood, cardboard and textiles. The solid resinous mass may be made into shaped articles under the application of heat and pressure. If the resin is dissolved in anhydrous acetic acid and mineral acid added, precipitation with water yields a yellow substance which will not fuse below 300°C.

Acetaldehyde resins are soluble in many organic solvents, but they are not soluble in aqueous solutions of borax and soda which is a characteristic of shellac that permits it to be employed in the manufacture of leather dressings. To make acetaldehyde resins soluble in alkaline solutions, Herrmann and Deutsch<sup>15</sup> subjected them to an oxidation treatment.<sup>16</sup> For instance, to 60 parts of 4 per cent aqueous caustic soda are added 200 parts of acetaldehyde. The temperature is kept for some time between 40-100°C. and the volatile components are distilled off. Further heating is continued at temperatures above 100°C. Ten parts of the resulting resin are dissolved in 100 parts of glacial acetic acid and ozonized oxygen is passed through the solution. When the oxidation has reached the degree desired, water is added which precipitates the resin. The oxidation may also be carried out with the resin in a molten state or when finely divided and suspended in water. Paquin, Voss and Wohlers<sup>17</sup> likewise gave related resins an oxidation treatment. They suspended or dissolved resinous products obtained by condensation of acetaldehyde, crotonaldehyde and aldol in inert media (alcohol or water) and oxidized them with chlorine or potassium chlorate and hydrochloric acid.

Heat treatment of acetaldehyde resins is said to raise the softening point and to increase the hardness, luster, elasticity and utility as varnish resins.<sup>18</sup> The method involves heating the resin at above 100°C. for several hours. Some inorganic metallic compounds<sup>19</sup> are also helpful; by stirring with aluminum hydroxide at 200°C. the softening point may be raised from 110°C. to 150°C.

By the addition of substances containing carboxyl and carbonyl groups,<sup>20</sup> acetaldehyde resins are said to have a better elasticity, solubility in alcohol and a lighter color; appropriate substances include dihydroxystearic acid, ricinoleic acid, dihydroxyabietic acid, mesityl oxide and salicylic acid. One method recommended is as follows: The resinous product obtained on condensing 500 parts of acetaldehyde by 300 parts of 20 per cent caustic soda solution is melted with 30 per cent of its weight of ricinoleic acid and kept in the molten state at 150°C. for a short time. It is rolled out in a milling apparatus to shellac-like sheets. The modifying agents may also be introduced during the resinification process. The resin thus prepared can also be melted with castor oil and further admixed with an alcohol-soluble polymerized vinyl acetate.<sup>21</sup>

<sup>15</sup> W. O. Herrmann and H. Deutsch, U. S. P. 1,489,213, Apr. 1, 1924, to Consort. für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1924, 18, 1917. Canadian P. 240,753, 1924; *Chem. Abs.*, 1924, 18, 2817.

<sup>16</sup> See *Chem. Met. Eng.*, 1924, 30, 522.

<sup>17</sup> M. Paquin, A. Voss and H. Wohlers, German P. 448,427, 1924, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1923, 867.

<sup>18</sup> H. Deutsch and W. O. Herrmann, German P. 381,720, 1920, to Consort. für elektrochem. Ind. G.m.b.H. Canadian P. 265,173, 1926; *Chem. Abs.*, 1927, 21, 1021.

<sup>19</sup> H. Deutsch and W. O. Herrmann, German P. 394,946, 1921, to Consort. für elektrochem. Ind. G.m.b.H.; *J.S.C.I.*, 1924, 43, 840B.

<sup>20</sup> W. O. Herrmann and H. Deutsch, German P. 422,538 and 433,853, 1922, to Consort. für elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B*, 1927, 228. See W. O. Herrmann, H. Deutsch and W. Haehnel, U. S. P. 1,643,496, Sept. 27, 1927; *Chem. Abs.*, 1927, 21, 2907. Canadian P. 249,338, 1925; *Chem. Abs.*, 1925, 19, 3381. British P. 201,916, 1923; *J.S.C.I.*, 1925, 44, 45B.

<sup>21</sup> W. O. Herrmann, H. Deutsch and W. Haehnel, U. S. P. 1,985,993, Jan. 1, 1935, to Chemische Forschungsge. m.b.H.

According to Herrmann and Deutsch,<sup>22</sup> acetaldehyde resins mixed with organic substances containing carboxyl groups may be utilized in the manufacture of linoleum. A resin having a softening point of 40-50°C. can be prepared by the partial condensation of acetaldehyde with sodium hydroxide. One hundred parts of such a resin were melted with 85 parts of castor oil and heated for 16 hours at 200°C. whereupon 100 parts of the resulting mix were kneaded thoroughly at 120-130°C. with 30 parts of ground ocher and 15 parts of cork flour. The plastic was calendered in the usual manner on a burlap base. By mixing with various other fillers together with synthetic and natural resins substitutes for cork, horn and ivory may be made.

Resins prepared from acetaldehyde and alkali are said to be improved by heating to 110°C. with polyvinyl acetate or other polyvinyl compounds.<sup>23</sup> Powdered alkali and resin when mixed and heating so arranged as to allow the greatest amount of hydrogen to be split off yielded salts of carboxylic acids.<sup>24</sup>

Acetaldehyde resins may be made soluble in fatty oils by heating them with oil-soluble natural resins (rosin) or by heating at 150-300°C. mixtures of the resins with fatty oils (linseed oil), until a sample remains homogeneous on cooling.<sup>25</sup> The products can be diluted with turpentine. Haehnel and Herrmann<sup>26</sup> rendered acetaldehyde resins soluble in weak alkalies by treatment with strong alkalies in the presence of fatty oils or hydroxy fatty acids derived from them. The treatment may be carried on at ordinary or elevated temperatures. Voss<sup>27</sup> heated the resins prepared by condensation of acetaldehyde with other natural or synthetic resins (rosin or cumarone) until the end product exhibited the solubility properties of the second component. Further hardening of aldehyde resins, after heat treatment, may be effected by esterification with glycerol.<sup>28</sup>

Herrmann, Deutsch and Haehnel<sup>29</sup> produce resins directly from acetylene by causing it to react upon catalyzers in the presence of water and continuing the reaction beyond the intermediate formation of acetaldehyde. An acetaldehyde condensation product is made by Shaw,<sup>30</sup> who reacts the aldehyde at 10-15°C. with 2.2 g. of alkali condensing agent per kg. of finished product (the condensing agent being an aqueous 10 per cent solution) and then treating the resulting mass at 20-45°C. with approximately double the amount of the same condensing agent in a solution of concentration of 20 per cent.

#### ACID RESINIFICATION

Wurtz<sup>31</sup> observed the resinification of acetaldehyde by hydrochloric acid. Herrmann and Deutsch<sup>32</sup> have prepared an aldehyde resin by using 25 per cent sulphuric acid. The temperature is kept at 40°C. for several hours; then raised

<sup>22</sup> W. O. Herrmann and H. Deutsch, U. S. P. 1,625,852, Apr. 26, 1927, to Consort für elektrochem. Ind.; *Chem. Abs.*, 1927, 21, 2072. Canadian P. 259,177, 1926; *Chem. Abs.*, 1926, 20, 3580.

<sup>23</sup> H. Deutsch, W. Haehnel and W. O. Herrmann, German P. 534,936, 1926, to Consort. für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, 26, 1143.

<sup>24</sup> W. Haehnel and W. O. Herrmann, German P. 588,762, 1933, to Consort. für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 2018.

<sup>25</sup> German P. 372,103, 1923, to Elektrizitätswerk Lonza A.-G.; *J.S.C.I.*, 1923, 42, 731A.

<sup>26</sup> W. Haehnel and W. O. Herrmann, German P. 502,432, 1927, to Consort. für elektrochem. Ind.; *Chem. Abs.*, 1930, 24, 4045.

<sup>27</sup> A. Voss, German P. 477,226, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 4090.

<sup>28</sup> British P. 187,619, 1922, to Consort für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1924, 18, 594.

<sup>29</sup> W. O. Herrmann, H. Deutsch and W. Haehnel, Canadian P. 256,556, 1925; *Chem. Abs.*, 1926, 20, 2333.

<sup>30</sup> G. S. Shaw, Canadian P. 281,951, 1928, to Can. Electro Products Co. Ltd.; *Chem. Abs.*, 1928, 22, 3498.

<sup>31</sup> A. Wurtz, "Dictionnaire de Chimie," Librairie Hachette et Cie, Paris, Supplement I, 87. *Rev. gen. chim.*, 1907, 10, 51.

<sup>32</sup> W. O. Herrmann and H. Deutsch, U. S. P. 1,600,113, Sept. 14, 1928, to Consort. für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1926, 20, 3581. British P. 187,619, 1922, to Consort. für elektrochem. Ind.; *J.S.C.I.*, 1923, 42, 730A.

to 100°C. The toughness and hardness of the product depends upon the duration of the heating. The resin obtained is said to be suitable for varnishes.

#### VARIOUS OTHER MEANS OF RESINIFICATION

Berthelot and Gaudechon<sup>38</sup> from a study of the photolysis of acetaldehyde vapor found that resinification results only slowly by the action of long ultraviolet rays. Continuing the work, Leighton and Blacet<sup>39</sup> determined that the absorption bands lie between 2730-3400 Å with a maximum at about 3100 Å and produce two reactions, one a decomposition giving principally carbon monoxide and the corresponding hydrocarbon,<sup>40</sup>  $R-CHO \rightarrow RH + CO$ , and the other a polymerization into complex products. The nature of the polymerization products is not stated, presumably they are a mixture of para- and metaldehyde. Other saturated aliphatic aldehydes when exposed to the rays of a quartz mercury lamp exhibited a certain degree of condensation or polymerization to resins.<sup>41</sup> Carbon monoxide was also evolved, a reaction which appears to apply only to this type of aldehyde since no gas was detected on irradiating crotonaldehyde, benzaldehyde and cinnamaldehyde.

Schweizer and Geilinger<sup>37</sup> suspect the existence in yeast of an enzyme aldehydase which brings about transformation of substances of the aldehyde group according to the Cannizzaro reaction. Experiments, in which the masking effect of oxygen was eliminated by means of alkaline pyrogallate, lent support to their view. Bodnar and Bernauer<sup>36</sup> found that pea meal converted acetaldehyde into acetaldol and aldehyde resins.

Slight resinification of acetaldehyde is reported by Urey and Lavin<sup>42</sup> in a study of the reactions of atomic hydrogen. The main reaction, however, is that of paraldehyde formation.

When mercuric nitrate acidified with nitric acid is added either to acetylene or to an alcoholic solution of acetaldehyde, a compound of the formula  $C_2HNO.Hg_2$  is obtained. On warming this mercury derivative with caustic soda or with potassium cyanide solution, a considerable amount of aldehyde resin is formed.<sup>43</sup>

Cyanamide dissolves in acetaldehyde and in 24 hours the resulting solution changes to a resinous body insoluble in water but soluble in alcohol. Ether precipitates the resin from alcohol.<sup>44</sup> Cyanamide reacts violently with chloral forming a sticky resin which hardens in air. This is moderately soluble in alcohol, ether and chloroform but becomes brown on heating and decomposes at 210°C.<sup>45</sup>

Vacuum distillation of the products of the reaction between cinnamic aldehyde and acetaldehyde, in the presence of sodium hydroxide, yields a black tar-like residue. Moreover, the reaction product of acetaldehyde and 5-phenyl-2,4-pentadienal-1, that is, 7-phenyl-2,4,6-heptatrienal-1, when oxidized with ammoniacal silver

<sup>38</sup> D. Berthelot and H. Gaudechon, *Compt. rend.*, 1910, 151, 478; 1913, 233, 68; *Chem. Abs.*, 1911, 5, 2629; 1912, 7, 1484. See Carleton Ellis and A. A. Wells, "Chemical Action of Ultraviolet Rays," *Chem. Catalog Co.*, New York, 1925, 155.

<sup>39</sup> P. A. Leighton and F. E. Blacet, *J.A.C.S.*, 1933, 55, 1766.

<sup>40</sup> A study of the thermal decomposition of gaseous acetaldehyde by C. N. Hinshelwood and W. K. Hutchison (*Proc. Roy. Soc.*, 1926, 111A, 380; *Chem. Abs.*, 1926, 20, 2774) revealed a smooth conversion at 501°C. into methane and carbon monoxide.

<sup>41</sup> A. Franke and E. Pollitzer, *Monatsh.*, 1913, 34, 797; *Chem. Abs.*, 1913, 7, 2543.

<sup>37</sup> C. Schweizer and H. Geilinger, *Mitt. Lebensm. Hyg.*, 1924, 15, 41; *Chem. Abs.*, 1924, 18, 2938.

<sup>36</sup> J. Bodnar and C. Bernauer, *Biochem. Z.*, 1929, 209, 458.

<sup>42</sup> H. C. Urey and G. I. Lavin, *J.A.C.S.*, 1929, 51, 3286.

<sup>43</sup> K. A. Hofmann, *Ber.*, 1898, 31, 2213, 2784.

<sup>44</sup> Knop, *Ann.*, 1864, 131, 253; "Beilstein's Handbuch der organischen Chemie," 4th Ed., 1921, III, 79.

<sup>45</sup> M. Fileti and R. Schiff, *Ber.*, 1877, 10, 426. G. Heim, (*Bull. soc. chim. Belg.*, 1903, 41, 320; *Chem. Abs.*, 1903, 27, 267) reports that the condensation of cyanoacetic acid in the presence of pyridine results in the production of 50 per cent of tarry material.

oxide to the corresponding acid, becomes partly resinified.<sup>44</sup> According to Rieche,<sup>44</sup> the reaction product of acetaldehyde and hydrogen peroxide is converted by phosphorus pentoxide in ether into a polymeric ethylidene peroxide.

Voss<sup>45</sup> has prepared a water-soluble viscous material by gently heating under reduced pressure the condensate of formaldehyde with acetaldehyde. Polymerized vinyl alcohol-acetaldehyde condensation products are obtained<sup>46</sup> by treating polymerized vinyl alcohols with aliphatic aldehydes such as formaldehyde or acetaldehyde in the presence of acid catalysts. The materials are said to be rubber-like, plastic and elastic or hard and brittle depending on the proportion of aldehyde.

In a study of condensation reactions of acetaldehyde over oxide catalysts at pressures of 1-500 atmospheres of hydrogen, Adkins, Kinsey and Folkers<sup>47</sup> report the production of some tar-like substance. In one experiment in which ethanol and acetaldehyde reacted under high pressure over a zinc chromite catalyst there was about 9 per cent of residue, after distillation of products up to 160°C. at 2 mm. pressure. Manganese chromite catalysts performed in about the same way as the zinc chromite. Copper chromite produced very little tar.

Bodendorf<sup>48</sup> has investigated the reaction of aliphatic aldehydes (1 mol) with a suspension of aluminum chloride (1.2 mols) in benzene saturated with dry hydrogen chloride. Fifty per cent yields of the corresponding diaryl paraffins were obtained. The by-products were alkylbenzenes and resinous materials.

#### USES OF ACETALDEHYDE RESINS

In addition to the uses for these resins already indicated, Osborn<sup>49</sup> suggests their use as dental impression compositions. Further uses are as agglutinants in the manufacture of micanite and other electrical insulating materials<sup>50</sup> and for photographic filters. A bright yellow light filter may be formed from cellulose ethyl ether and acetaldehyde resin.<sup>51</sup> Bradshaw<sup>52</sup> made a casein glue by the addition of polymerized acetaldehyde to a dry glue base containing casein, hydrated lime and alkali salts.

#### ACETALS

Acetal, when kept out of contact with air, does not react with alkali at ordinary or at higher temperatures.<sup>53</sup> In the presence of air, however, or in alcoholic potash solution, acetal readily darkens with the formation of a dark resin.<sup>54</sup> Acetylene, which functions as anhydrous acetaldehyde, may be hydrated to acetaldehyde by means of a catalyst consisting of mercuric sulphate and sulphuric acid. Similarly, alcoholation yields acetals, i.e., diethyl acetal is formed in the case of ethyl alcohol. On continued passage of acetylene, however, crotonaldehyde appears as an intermediary and the final product is a black resin. Fusel oil, when treated in the same

<sup>44</sup> D. Vorländer, E. Fischer and K. Kunze, *Ber.*, 1925, 58, 1284.

<sup>45</sup> A. Rieche, *Ber.*, 1931, 64, 2328.

<sup>46</sup> A. Voss, U. S. P. 1,878,040, Sept. 20, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 381. French P. 690,688, 1930; *Chem. Abs.*, 1931, 25, 1845.

<sup>47</sup> British P. 337,806, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2253.

<sup>48</sup> H. Adkins, M. E. Kinsey and K. Folkers, *Ind. Eng. Chem.*, 1930, 22, 1046.

<sup>49</sup> K. Bodendorf, *J. prakt. Chem.*, 1931, 129, 337; *Chem. Abs.*, 1931, 25, 2698.

<sup>50</sup> H. Osborn, British P. 368,622, 1931, to Associated Products, Ltd.; *Brit. Chem. Abs. B*, 1932, 475.

<sup>51</sup> British P. 220,949, 1924, to Consort. für elektrochem. Ind.; *J.S.C.I.*, 1925, 44, 639B.

<sup>52</sup> British P. 293,350, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 1750.

<sup>53</sup> L. Bradshaw, U. S. P. 1,895,433, Jan. 24, 1933; *Chem. Abs.*, 1933, 27, 2542.

<sup>54</sup> Stas, *Ann. chim. phys.*, 1830-4, 19, 146. *J. prakt. Chem.*, 1846, 40, 340.

<sup>55</sup> J. Liebig, *Ann.*, 1835, 5, 25; 1835, 14, 186; *Annales der Physik u. Chemie, von Poggendorf*, 1833, 27, 605. L. Gmelin, "Handbook of Chemistry," Cavendish Society, London, 1855, 9, 38.

manner, quickly thickens into a jelly-like mass which hardens into a solid body resembling hard rubber.<sup>55</sup>

Methylal is produced in 97 per cent of the calculated yield by reacting 2 mols of methanol with 1 mol of trioxymethylene in the presence of ferric chloride. The latter is the most effective of the many catalysts examined. All the catalytically active salts examined were capable of forming alcoholates. The catalysts did not induce polymerization of the aldehyde during the usual time involved in the acetal reaction.<sup>56</sup>

#### MANUFACTURE OF ACETALDEHYDE

Much difficulty is experienced in the synthesis of acetaldehyde from acetylene<sup>57</sup> inasmuch as the reaction is carried out in acid solution which is an appropriate medium for the formation of aldehyde resins.

Formation of resinous matter when working at temperatures of 70-90°C. is avoided by using as catalyst for the conversion, an aqueous solution of an alkali hydrogen sulphate, containing a mercury compound and a compound of a metal of group I or VIII.<sup>58</sup>

In another method, resinification is avoided by continuously circulating the liquid between the reaction chamber and another chamber where the aldehyde formed is isolated by vacuum distillation.<sup>59</sup>

Continuous and regular formation of acetaldehyde was effected by Ledru and Bachmann<sup>60</sup> using a mercury salt as a catalyst in the oxidation of acetylene. A mixture of acetylene and 2-20 per cent of oxygen was allowed to stream through a stirring apparatus containing 4.3 kg. of 100 per cent sulphuric acid, 1 kg. of ferrous sulphate, 0.300 kg. of mercury, 0.150 kg. of crystalline copper sulphate and 16 l. of water. Acetic acid is also produced.

Snow and Keyes<sup>61</sup> investigated the influence of about 150 substances upon the partial oxidation of liquid ethyl alcohol both at atmospheric pressure (72°C.) and at 170 pounds per square inch (100°C.). Compared with vapor-phase oxidation, better temperature control is possible in the liquid phase owing to the high specific heat. Alcohol containing a catalyst in suspension or solution was placed above the porous plate of a Schott filter funnel kept at 70-75°C. by steam heat, and oxygen was forced through the plate. No acetic acid was formed at atmos-

TABLE 30.—*List of Substances Having Catalytic Activity.*

Group of the Periodic Table	Substances Which Catalyze the Oxidation of Alcohol to Aldehyde.
I	Copper and copper-zinc couple.
II	Soluble salts of mercury, zinc and cadmium.
III	Soluble salts of aluminum and metallic boron, aluminum and indium.
IV	Soluble salts of lead, tin and titanium, also the corresponding metals.
V	Vanadium pentoxide and acetate, phosphotungstic and phosphomolybdic acids, also phosphorus pentoxide.
VI	Chromous acetate, potassium dichromate, chrome alum and selenious acid.
VII	Manganese acetate, sulphate, oxide and metallic manganese.
VIII	Soluble salts of iron, cobalt and nickel, also metallic palladium, iron, cobalt and nickel.

<sup>55</sup> J. S. Reichert, J. H. Bailey and J. A. Nieuwland, *J.A.C.S.*, 1923, 45, 1552.

<sup>56</sup> E. W. Adams and H. Adkins, *J.A.C.S.*, 1925, 47, 1358.

<sup>57</sup> Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 666, 667, 835.

<sup>58</sup> British P. 312,716, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1929, 670.

<sup>59</sup> Alais, Froges and Camargue Co., *Chem. Age (London)*, 1925, 13, 279; *Cf. ibid.*, 1923, 9, 230.

<sup>60</sup> M. J. L. Ledru and E. J. Bachmann, *U. S. P.* 1,532,190, Apr. 7, 1925, to Soc. chim. usines du Rhone; *J.S.C.I.*, 1925, 44, 525B.

<sup>61</sup> R. D. Snow and D. B. Keyes, *Ind. Eng. Chem.*, 1931, 23, 561.



pheric pressure and acetaldehyde represented the limit of oxidation except in one instance. Cerium oxide in the presence of alkali led to formation of acetic acid, formic acid, acetaldehyde resin and carbon dioxide. A list of some of the other substances which exhibited catalytic activity is given in Table 30 (on page 496). Rare earths were ineffective but hopcalite (a combination of manganese, copper, silver and cobalt) was quite active. Good results were obtained with hopcalite and cerous hydroxide in sodium carbonate solution.

#### ACETALDOL AND CROTONALDEHYDE

One of the chief drawbacks in aldolization, according to Kyriakides,<sup>62</sup> is the fact that both aldehydes and aldols<sup>63</sup> are sensitive to alkalis so that there is more or less resinification during the reaction.<sup>64</sup> The older investigators circumvented the difficulty by using very mild alkaline reagents to effect the condensation; the later methods are to use strong alkali in the presence of organic solvents. Through this means the aldol is continually extracted from the sphere of further action of the alkali. Grignard and Rief<sup>65</sup> used sodium sulphite and large amounts of ether. Hibbert<sup>66</sup> dissolved acetaldehyde in gasoline and treated the solution, after cooling to  $-10^{\circ}\text{C}.$ , with sodium or potassium hydroxide. The end-point of the condensation may be judged by the light yellow color in the aldol liquid. This color is a sign of the formation of higher condensation products. For maximum yield of the aldol, the liquid should be colorless at the end of the reaction.

Grünstein<sup>67</sup> effected aldolization without using a solvent. Acetic acid in the aldehyde was first neutralized with sodium hydroxide and an alkaline catalyst was introduced with cooling. A small amount of water appeared to be essential. To prevent the condensation from going too far, acid was added and the products distilled *in vacuo*.

To produce acetaldol, Matheson<sup>68</sup> added 1.3 cc. of a 10 per cent caustic soda solution slowly with stirring and cooling to 200 g. of acetaldehyde which had been previously cooled to about  $-25^{\circ}\text{C}.$  The initial reaction was very vigorous and the material had to be kept below  $10-20^{\circ}\text{C}.$  in order to prevent resinification. After 30 minutes, the material was a thick colorless product from which the remaining aldehyde and water were distilled. The aldol could be distilled *in vacuo*. Other investigators aldolize aqueous acetaldehyde in the presence of alkali, keeping the temperature at  $15^{\circ}\text{C}.$ <sup>69</sup> or below, or pass the acetaldehyde and condensing agent through reaction chambers provided with cooling coils.<sup>70</sup>

Herrly<sup>71</sup> stated that the reaction is more easily controlled when the alkali concentration is low and the temperature is high. According to his directions, the acidity of the acetaldehyde, which is due to organic acid impurities, is first

<sup>62</sup> L. P. Kyriakides, *J.A.C.S.*, 1914, 36, 352.

<sup>63</sup> Aldols form a complex with "dimedon" (dimethyldihydro-resorcinol) which can be differentiated from the analogous acetaldehyde complex by its insolubility in light petroleum. See R. Fricke, *Z. Physiol. Chem.*, 1921, 116, 129; *J.S.C.I.*, 1922, 41, 268A.

<sup>64</sup> M. C. Reed (U. S. P. 1,763,326, June 10, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 3799) has found that the addition of a small amount of secondary aromatic amine (phenyl- $\beta$ -naphthyl amine) effects the stabilisation of butyraldehyde. Resinification may be avoided in the preparation of cyanohydrins of aliphatic or aromatic aldehydes or ketones, or of alkylene oxides, when the reaction takes place in the presence of an organic base of a concentration of 0.1-1.0 per cent of the hydrogen cyanide. See British P. 359,262, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 173.

<sup>65</sup> V. Grignard and J. Rief, *Bull. soc. chim.*, 1907 (4) 1, 114; *Chem. Abs.*, 1907, 1, 1389.

<sup>66</sup> H. Hibbert, U. S. P. 1,068,048, Feb. 3, 1914; *Chem. Abs.*, 1914, 8, 1190.

<sup>67</sup> N. Grünstein, British P. 147,119, 1920; *J.S.C.I.*, 1922, 41, 78A. British P. 101,636, 1916; *J.S.C.I.*, 1917, 36, 1064.

<sup>68</sup> H. W. Matheson, U. S. P. 1,450,984, Apr. 10, 1923, to Can. Electro Products Co., Ltd.; *Chem. Abs.*, 1923, 17, 1969. Canadian P. 228,441, 1923; *Chem. Abs.*, 1923, 17, 1241.

<sup>69</sup> British P. 274,488, 1927, to Distilleries des Deux-Sevres; *Brit. Chem. Abs. B*, 1928, 921.

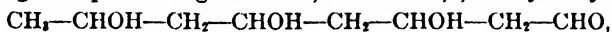
<sup>70</sup> British P. 298,349, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 2725.

<sup>71</sup> C. J. Herrly, U. S. P. 1,598,532, Aug. 31, 1926, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1926, 20, 3461.



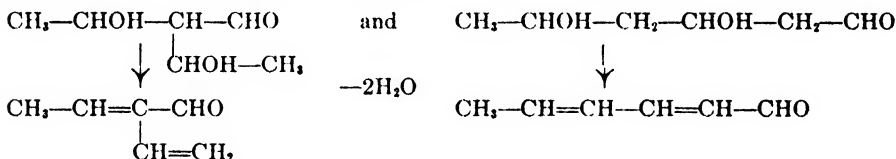
By heating dialdan with aqueous ammonia under pressure at 100°C., a resinous body is obtained which is crystallizable and which possesses the formula,  $C_{10}H_{20}N_2O_4$ . It is soluble in ether, alcohol and water. Its aqueous solution is alkaline, however, and long standing in water causes an amorphous body to settle out.<sup>64</sup>

Hammersten<sup>65</sup> observed that aldol does not disappear during resin formation even at higher temperatures or at longer reaction times. The first condensation product is changed in part to higher aldols, of which 3,5,7-trihydroxy-1-octanal,



has been isolated. In no experiment, under the conditions reported, was less than 40 per cent of aldol obtained from 0.5 *N* acetaldehyde solution. This may be taken to mean that the higher aldols do not form aldehyde resins. With higher concentrations of alkali the Cannizzaro conversion was more pronounced than with lower concentrations; this was the case with potassium hydroxide. With barium hydroxide, the concentration was not so important. Lead hydroxide had a specific action since noticeable aldol formation took place, but neither the Cannizzaro effect nor resin formation occurred.

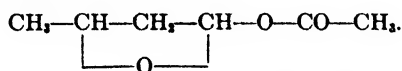
An instructive condensation in this connection has been worked out by Zeisel and Neuwirth<sup>66</sup> for the autocondensation of acetaldehyde in the presence of sodium acetate. The action is shown as follows:



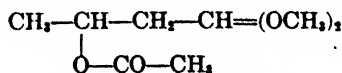
Both  $\alpha$ -vinyl crotonaldehyde (2-vinyl-2-butenal-1) and sorbaldehyde (2,4-hexadienal-1) were isolated and their boiling points at 24 mm. are 55-60°C. and 75-80°C., respectively. Both substances resinify easily.

Aldol can be polymerized in the presence of either calcium or magnesium oxide without the formation of insoluble resins if the temperature is maintained under 70°.<sup>67</sup> Resins are obtained, however, when the mixture remains alkaline to phenolphthalein during the reaction. Under these conditions a compound of approximately twelve carbon atoms to the molecule is formed.<sup>68</sup>

Treatment of acetal with cold acetic anhydride in presence of pyridine was found by Bergmann and Kann<sup>69</sup> to lead to formation of acetylcycloaldol or paral-dol diacetate (b.p. 156-158°C. at 12 mm.),



It yields a colorless viscous oxime boiling at 120-122°C. at 12 mm. In the same way, aldol-dimethylacetal yields acetylaldoldimethylacetal (b.p. 84-86°C. at 13 mm.),



<sup>64</sup> A. Wurts, *Compt. rend.*, 1880, 91, 1030; *Chem. Zentr.*, 1881, 69; *Jahresbericht*, 1880, 524.

<sup>65</sup> H. Hammersten, *Ann.*, 1920, 421, 293.

<sup>66</sup> S. Zeisel and M. Neuwirth, *Ann.*, 1923, 433, 121; *Chem. Abs.*, 1924, 18, 58.

<sup>67</sup> J. V. Eyre and H. Langwell, British P. 416,734, 1930, to The Distillers Co., Ltd.; *Chem. Abs.*, 1935, 29, 1162. French P. 770,210, 1934; *Chem. Abs.*, 1935, 29, 476.

<sup>68</sup> J. V. Eyre and H. Langwell, British P. 411,433, 1932, to The Distillers Co., Ltd.; *Brit. Chem. Abs.*, 1934, 726. French P. 763,784, 1934; *Chem. Abs.*, 1934, 28, 5693.

<sup>69</sup> M. Bergmann and E. Kann, *Ann.*, 1924, 436, 278; *Chem. Abs.*, 1924, 18, 3358.

This substance is hydrolyzed to 3-acetoxybutanol, which forms the same oxime as the above acetylcycloaldol. The tendency to polymerization of the aldolcycloacetates was ascribed to the unsaturated affinity of the bridge oxygen and is more pronounced the shorter the space between the two carbon atoms thereby linked.

The action of hydrochloric acid on acetaldol produced resinification as well. Glassy solids have been prepared in this manner.<sup>90</sup> In studying methods for preparing 1,2-dimethylcyclopropanes, Baudrenghien<sup>91</sup> obtained solely resinous products on treating aldol with hydrochloric acid.

#### CROTONALDEHYDE

Crotonaldehyde, which, as has been previously indicated, is a dehydration product of acetaldol, is formed when the aldol is acidified with a weak mineral acid.<sup>92</sup> It can also be produced by means of catalysts. Thus, aldol may be converted to crotonaldehyde in alkaline solution by heating with salts of organic acids.<sup>93</sup> Herrly<sup>94</sup> introduced aldol into a heated zone in a current of nitrogen, steam or other inert gaseous medium in order to prepare crotonaldehyde. Acetaldehyde vapor may be passed over catalysts such as charcoal coated with titanium oxide or masses of aluminum hydroxide to produce crotonaldehyde.<sup>95</sup> Brus<sup>96</sup> produced crotonaldehyde from alcohol by the action of anhydrous zinc sulphate, the alcohol being dehydrogenated to the aldehyde, condensed to aldol and dehydrated to crotonaldehyde.<sup>97</sup>

Crotonaldehyde forms a resin in both alkali and acid.<sup>98</sup> When dissolved in ether and treated with ethereal hydrogen bromide at  $-5^{\circ}\text{C}.$ , crotonaldehyde forms highly polymerized products.<sup>99</sup> Treatment of this aldehyde with sodium amalgam also causes resinification.<sup>100</sup> A resinous product is produced from crotonaldehyde and an aromatic amine.<sup>101</sup> For example, to 56 parts by weight of crotonaldehyde, 60 parts by weight of aniline are gradually added with stirring. The temperature during the process is not allowed to exceed  $50^{\circ}\text{C}.$  When all the aniline has been added, the reaction mass is further stirred for 3 hours at this temperature whereupon it is allowed to stand over night. The residue obtained by vacuum distillation of the volatile constituents is a brittle resin.

On passing oxygen through crotonaldehyde at  $70^{\circ}\text{C}.$  for several days, crotonic acid may be obtained together with acetic acid and a resinous condensation product.<sup>102</sup> Resin formation as a result of oxidation of crotonaldehyde with gaseous oxygen has also been recorded by Young<sup>103</sup> who agitated the reaction mixture in a closed system at a temperature reaching  $50-90^{\circ}\text{C}.$ , for 10-15 minutes. By maintaining the temperature below  $30^{\circ}\text{C}.$ , resin formation was largely avoided.

<sup>90</sup> A. Wurtz, "Dict. de chimie," Supplement I, 87; *Rev. gen. chim.*, 1907, 10, 51.

<sup>91</sup> J. Baudrenghien, *Bull. sci. acad. roy. Belg.*, 1929, 15, 53; *Chem. Abs.*, 1929, 23, 4196.

<sup>92</sup> G. F. Horsley, British P. 313,466, 1928, to Imperial Chem. Ind. Ltd.; *Brit. Chem. Abs. B*, 1929, 672. British P. 274,488, 1927, to Distilleries des Deux-Sevres; *Brit. Chem. Abs. B*, 1928, 921.

<sup>93</sup> J. Sieb, British P. 320,210, 1928, to Holzverkohlungs-Ind. A.-G.; *Brit. Chem. Abs. B*, 1930, 315. See E. Lüscher, U. S. P. 1,693,907, Dec. 4, 1929, to Electricitätswerke Lonza; *Chem. Abs.*, 1929, 23, 850; *Brit. Chem. Abs. B*, 1929, 47. British P. 270,764, 1926; *Chem. Abs.*, 1928, 22, 1596.

<sup>94</sup> C. J. Herrly, U. S. P. 1,585,096, May 18, 1926, to Carbide & Carbon Chem. Corp. British P. 242,521, 1925; *Chem. Abs.*, 1926, 20, 2167.

<sup>95</sup> German P. 349,915, to Consort. für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1923, 17, 1249.

<sup>96</sup> G. Brus, *Bull. soc. chim.*, 1923, 33, 1433.

<sup>97</sup> N. H. Johanson (British P. 185,126, 1922; *Chem. Abs.*, 1923, 17, 179) suggests crotonaldehyde thus prepared be used as an alcohol denaturant.

<sup>98</sup> A. Wurtz, *Bull. soc. chim.*, 1880, (2) 34, 486; *Compt. rend.*, 1872, 74, 1361; *Chem. Zentr.*, 1872, 483.

<sup>99</sup> R. Lespieau and R. L. Wakeman, *Bull. soc. chim.*, 1932, 51, 384.

<sup>100</sup> A. Lieben and Zeisel, *Monatsh.*, 1880, 1, 823; cf. "Beilstein's Handbuch der organischen Chemie," 4th Ed., 1918, I, 729.

<sup>101</sup> W. Kropp, U. S. P. 1,640,899, Aug. 30, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1927, 21, 3474. See German P. 372,855, 1920, to K. Daimler; *J.S.C.I.*, 1928, 42, 1140A.

<sup>102</sup> A. Duclaux and M. Delepine, *Bull. soc. chim.*, 1924, 35, 1311.

<sup>103</sup> W. G. Young, *J.A.C.S.*, 1932, 54, 2498.

Tricrotonylidenetetramine,  $C_{12}H_{24}N_4$ ,<sup>104</sup> is made by heating crotonaldehyde or acetaldo with ammonia. On heating the amine with hydrochloric acid, a resin is formed together with ammonium chloride.<sup>105</sup> Crotonaldehyde phenylhydrazine is decomposed by glacial acetic acid into a resin and acetylphenylhydrazine.<sup>106</sup> The reaction of crotonaldehyde with sodamide in ether produces resinous material.<sup>107</sup>

#### ACROLEIN

Acrolein, or acraldehyde,  $H_2C=CH-CHO$ , is usually made from glycerol.<sup>108</sup> Like many aldehydes it forms a number of polymerization products, but little is known concerning their structure. The polymers are ordinarily white and amorphous, although a powder and a gel have been prepared.

Acrolein changes easily to a white amorphous product, known as "disacryl," which is insoluble in water, acids, alkalis or alcohol. The effect of light, oxygen and inhibitors on the transformation of acrolein to disacryl has been studied by Moureu, Dufraisse and associates<sup>109</sup> in connection with their work on anti-oxygenes and negative catalysis. Acrolein is stable in the absence of oxygen and light. Upon exposure to light, however, disacryl is produced immediately, the change being detectable by cloudiness. The speed of the condensation can be increased about 500,000 times by bright sunlight; the variation in rate is not proportional to that of the illumination. Of the portions of the visible spectrum, indigo produced the most rapid condensation to disacryl; violet somewhat less. Disacryl is also produced when acrolein is exposed to oxygen even in complete darkness: very small amounts of oxygen are said to be effective (1:1,000,000). According to Moureu and Dufraisse the catalysis is due to a compound formed by acrolein with oxygen. When light and oxygen act together their action is not mutually complementary but rather inhibitory. Many phenols such as quinol and pyrogallol prevent the condensation, shielding acrolein from the effect of both light and oxygen.

McLeod<sup>110</sup> found that alkaline substances greatly accelerated the polymerization of acrolein. One of his experiments is as follows: to 23.5 g. of acrolein dissolved in 184 cc. of cold water was added 0.1 g. of potassium carbonate in 2 g. of water. An immediate turbidity occurred and a voluminous white substance soon separated with marked evolution of heat. After 18 hours, the odor of acrolein had disappeared; further addition of 0.1 g. of potassium carbonate was made and after 24 hours standing the products of polymerization were found to weigh 22.5 g. The polymer softened at 83°C. and decomposed with gas evolution at 94-95°C. A strong odor of acrolein was observed on warming with dilute acids or alkalis or on heating alone to 100°C. Like disacryl, McLeod's polymer is insoluble in water and glacial acetic acid; it is also insoluble in carbon bisulphide, benzene, ether and petroleum ether, but dissolves in warm 95 per cent alcohol. The polymer is insoluble in aqueous sodium carbonate; in 10 per cent aqueous sodium hydroxide a red-colored solution results. Digestion of this solution for a short time at 100°C. and subsequent neutralization with hydrochloric acid precipitates an amorphous substance of a very high melting point, the weight of which is about one-half of that of the polymer in solution.

<sup>104</sup> M. Delepine, *Compt. rend.*, 1907, 144, 853; *Chem. Abs.*, 1907, 1, 2087.

<sup>105</sup> A. Wurts, *Compt. rend.*, 1897, 88, 1154; *Chem. Zentr.*, 1879, 521.

<sup>106</sup> R. Wegscheider and E. Späth, *Monatsh.*, 1910, 31, 997; *Chem. Abs.*, 1911, 5, 1773.

<sup>107</sup> F. G. Fisher and K. Lowenberg, *Ann.*, 1932, 494, 263; *Chem. Abs.*, 1932, 26, 3498.

<sup>108</sup> T. Hanyu and T. Yanagibashi (*J. Soc. Chem. Ind., Japan*, 1934, 37, 538B; *Chem. Abs.*, 1935, 29, 727) have investigated the efficacy of ferric phosphate impregnated in pumice stone together with Japanese clay as dehydrating catalysts in the manufacture of acrolein from glycerol.

Commercial acrolein can be shipped and stored without resinifying and is therefore a recommended raw material both for soluble varnish resins and insoluble hard resins. See *Kunststoffe*, 1924, 14, 184.

<sup>109</sup> C. Moureu and C. Dufraisse, *Bull. soc. chim.*, 1922, (4) 31, 1152; 1924, (4) 35, 1564, 1572, 1591; *Chem. Abs.*, 1923, 17, 2105; 1923, 19, 1120. C. Moureu, C. Dufraisse and B. Badoche, *Compt. rend.*, 1924, 179, 1229; *Chem. Abs.*, 1925, 19, 1125.

<sup>110</sup> A. F. McLeod, *Am. Chem. J.*, 1907, 37, 20; *Chem. Abs.*, 1907, 1, 717.

Nef<sup>111</sup> obtained from acrolein in the presence of barium hydrate a polymer which softened at 115°C. and decomposed at 128-130°C. When dissolved in 10 per cent sodium hydroxide solution and heated, Nef's polymer gave rise to the same end product as that obtained by McLeod. None of the products obtained by McLeod or by Nef could be crystallized.

Moureu and Dufraisse<sup>112</sup> further investigated the resinification of acrolein in the presence of aqueous alkali and other catalytic agents. Instead of allowing the reactants to stand for a time (McLeod's procedure) they immediately filtered, washed and dried *in vacuo* the voluminous precipitate which is formed when a resinifying agent is added to an aqueous solution of acrolein. They obtained a white powder which is insoluble in water and hydrocarbons, but very soluble in the cold in many organic solvents, particularly alcohols, ketones and acids. The products formed by this method are said to have better solubility than those of McLeod. The resin in powdered form agglomerates to a viscous mass at temperatures between 80-110°C.

Other reagents which bring about the polymerization of acrolein to resin are potash, soda, lime, lead hydroxide, ammonia, methylamine, aniline, ferric chloride, lead acetate and hexamethylenetetramine-triphenol.<sup>113</sup>

Moureu and Dufraisse<sup>114</sup> state that pure acrolein, which at ordinary temperatures is a mobile liquid, changes under the influence of certain alkaline reagents into a viscous liquid which slowly passes into a solid resinous substance. This process, which has been referred to as a gelation, has been studied by Tampier and Gailliot,<sup>115</sup> who find that a large number of substances, but especially free alkalies and carbonates, catalyze the reaction. During the gelation the volume decreases about 25 per cent and heat is evolved. The change in density takes place rapidly during the first 10-15 days and continues slowly for months. It was also found that the electrical resistance of the gel increases linearly with its age.

No one, so far as is known, has investigated the structural relations<sup>116</sup> between disacryl, the polymer obtained in aqueous alkaline solution and the gelation product. Moureu and Dufraisse<sup>117</sup> state that disacryl formation and the conversion of pure liquid acrolein are two distinct reactions and take place concurrently. They also state that while oxygen has a catalytic effect on the formation of disacryl it has no effect at all on the other reaction.

An examination of the regular series of lines resembling furrows produced on the cut surface of an acrolein gel indicated that the greater part of the incident light is diffracted. It is believed that these furrows are present in the gel before fracture and consist of fine fissures (less than 0.5  $\mu$  long).<sup>118</sup> In common with other amorphous substances, acrolein resin exhibits the phenomenon of "amorphous expansion." This is due to an increase in the coefficient of expansion and not to the change of dimensions at the transition point; the latter phenomenon is typical of allotropic transformations.<sup>119</sup>

<sup>111</sup> J. U. Nef, *Ann.*, 1904, 335, 220; *J.C.S.*, 1905, 88 (1), 3.

<sup>112</sup> C. Moureu and C. Dufraisse, *British P.* 141,058, 1920; *J.S.C.I.*, 1921, 40, 858A. *Compt. rend.*, 1919, 169, 621; *Chem. Abs.*, 1920, 14, 401.

<sup>113</sup> T. Hanyu and T. Yanagihashi, *Researches Electro-tech. Lab., Tokyo, Japan*, 1930, (287), 18; *Chem. Abs.*, 1930, 24, 5515.

<sup>114</sup> C. Moureu and C. Dufraisse, *J.S.C.I.*, 1923, 47, 819, 848; 1929, 48, 736.

<sup>115</sup> L. Tampier and P. Gailliot, *J. phys. radium*, 1924, 5, 161; *Chem. Abs.*, 1924, 18, 3305.

<sup>116</sup> E. Hügglung (*Cellulosechemie*, 1925, 6, 29; *Chem. Abs.*, 1925, 19, 2327) believes that an acrolein residue may exist in  $\alpha$ -lignin. For a review of the chemistry of lignin, see M. Phillips, *Chem. Reviews*, 1934, 14, 103.

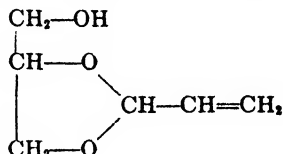
<sup>117</sup> C. Moureu and C. Dufraisse, *J.S.C.I.*, 1923, 47, 819, 848; 1929, 48, 736.

<sup>118</sup> C. Dufraisse and P. Gailliot, *Compt. rend.*, 1926, 183, 967; *Chem. Abs.*, 1927, 21, 1044.

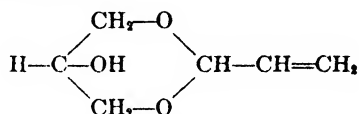
<sup>119</sup> M. O. Samsoen, *Ann. phys.*, 1928, 9, 35; *Chem. Abs.*, 1928, 22, 1851.

## ACRYLIDENE GLYCEROL

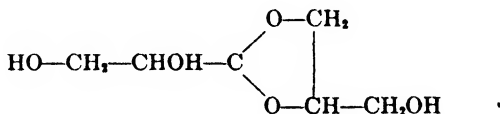
Hibbert and Whelen<sup>120</sup> have brought evidence to show that the non-polymerizable product of reaction between glycerol and acrolein without a catalyst under low pressure (repetition of Nef's work)<sup>121</sup> possesses the following structure:



A second isomer is possibly formed as required by Michael's partition principle but no doubt undergoes spontaneous polymerization and remains in the viscous undistillable residue which is always left in large proportion. In the monomeric form it would possess the structure:



The methyl ether of 1,2-acrylidene-glycerol is described as a mobile liquid, monomolecular in the freshly prepared condition but changing after several months into a viscous product (probably a dimer). Polymerization with subsequent ring closure is mentioned as one possible cause of the change. Distillation of 1,2-acrylidene-glycerol results in the formation of a large amount of unidentifiable caramel-like, dark brown residue. Attempts to polymerize 1,2-dihydroxypropylidene-glycerol



were unsuccessful. Hibbert and Whelen subjected the compound for several weeks to a temperature of 110°C. in the presence of various non-acid catalysts. No polymerization was observed. Negative results also followed prolonged heating in the absence of a catalyst or exposure to sunlight in a quartz glass tube. Nor was any tendency to polymerization observed in the case of the methyl ether. These facts are interesting on account of the relationship of the substances to cellulose and other polysaccharides.

Aqueous or alcoholic potash or silver oxide react with acrolein to form a yellow amorphous substance insoluble in water and soluble in alkalis, alcohol and ether.<sup>122</sup> A brown resin is formed when acrolein is heated for several days with 2-4 volumes of water at 100°C.<sup>123</sup> The product is somewhat soluble in water and easily soluble in alcohol or ether. Aeraldehyde reacts with ammonia to form a red amorphous substance easily soluble in water and acids.<sup>124</sup> By the

<sup>120</sup> H. Hibbert and M. S. Whelen, *J.A.C.S.*, 1929, 51, 3115.

<sup>121</sup> J. U. Nef, *Ann.*, 1904, 335, 224.

<sup>122</sup> A. Claus, *Ann.*, 1864, Spl. 2, 120. Beilstein, "Handbuch der organischen Chemie," 4th Ed., 1913, I, 726.

<sup>123</sup> A. Geuther, Cartmell, *Ann.*, 1859, 112, 10. Beilstein, "Handbuch der organischen Chemie," 4th Ed., 1913, I, 736.

<sup>124</sup> A. Claus, *Ann.*, 1864, 130, 186. Beilstein, "Handbuch der organischen Chemie," 4th Ed., 1913, I, 737.

action of water, lead oxide and silver carbonate on the cyclopropene dibromide, acrolein and polymers are formed. With water, above 150°C. a hard dark resin containing oxygen resulted.<sup>125</sup>

Auwers and Kreuder<sup>126</sup> mixed phenylhydrazine and acrolein and obtained a high proportion of resinous bodies. Tiglic aldehyde ( $\alpha,\beta$ -dimethylacetaldehyde) and phenylhydrazine when heated in the presence of acetic acid also yielded a resin. Lankelma and Sharnoff,<sup>127</sup> in a study of the reactions of 2-amino-4-chlorothiophenol with aldehydes, obtained only resinous products with unsaturated aldehydes.

Complete transformation, that is, in 100 per cent yield to a resin suitable as an ingredient of varnishes, is obtained by Moureu and Dufraisse<sup>128</sup> by condensing phenol and anhydrous acrolein in the presence of a very small proportion of an alkali catalyst. On bringing into contact, for example, 10 parts of commercial phenol and 90 parts of anhydrous acrolein in the presence of 1 part caustic soda, spontaneous resinification takes place at ordinary temperature, but is accelerated by heating at a temperature not exceeding 100°C. The reaction may also be carried out in a solvent and the proportion of acrolein can be varied as desired from 90 per cent (as in the above example) down to 20 per cent. Hydroxyphenylacroleins readily resinify in the presence of alkali hydroxide.<sup>129</sup> The resin-forming tendency can be suppressed by transformation of the hydroxyl group into the methoxy-methoxy-residue,  $\text{CH}_3\text{—O—CH}_2\text{—O—}$ .

Ushakov and Obriadina<sup>130</sup> used either mercuric or copper sulphate as catalysts in the formation of aldehydic resins from glycerol.<sup>131</sup> These resins, when used in conjunction with phenol resins, are said to impart elastic properties to the latter.

Polymerization of glycerol or other higher polyhydric alcohols with aqueous mercuric chloride or sulphate, cuprous chloride or ferric chloride leads to the formation of substances which may be used as explosion-proof lubricants for oxygen cylinders.<sup>132</sup>

### USES OF ACROLEIN RESINS

The polymers made by Moureu and Dufraisse<sup>133</sup> when dissolved in organic solvents can be used as varnishes. Acrolein resins possess good insulating properties. One sample gave volume resistance (23°C.)  $6 \times 10^{15} \sim 10^{16}$  ohms cm., surface resistance (humidity 90 per cent)  $10^{15} \sim 10^6$  ohms, dielectric constant  $4.06 \sim 4.32$ .<sup>134</sup> Work on the insulating power of acrolein gels has also been conducted by Tampier and Gailliot.<sup>135</sup> The so-called "Orca" resins of industry are formed from glycerol and are probably acrolein condensation products.<sup>136</sup>

Acrolein derivatives which act as accelerators of rubber vulcanization and as

<sup>125</sup> N. Ya. Dem'yanov and M. N. Doyarenko, *Bull. acad. sci. union rep. soviet social., Classe sci. phys. math.*, 1929, (7), 653; *Chem. Abs.*, 1930, 24, 1848.

<sup>126</sup> K. v. Auwers and A. Kreuder, *Ber.*, 1925, 58, 1974.

<sup>127</sup> H. P. Lankelma and P. X. Sharnoff, *J. A. C. S.*, 1932, 54, 379.

<sup>128</sup> C. Moureu and C. Dufraisse, *U. S. P.* 1,607,293, Nov. 16, 1926; *Brit. Chem. Abs. B*, 1927, 85; *British P.* 141,058, 1920; *J. S. C. I.*, 1921, 40, 853A.

<sup>129</sup> H. Pauly and K. Wascher, *Ber.*, 1923, 56, 603; *J. C. S.*, 1923, 124 (1), 342.

<sup>130</sup> S. N. Ushakov and E. M. Obriadina, *Ind. Eng. Chem.*, 1933, 25, 997.

<sup>131</sup> E. V. Zappi and R. A. Labriola (*Adhes. asoc. quim. Argentina*, 1930, 18, 243; *Chem. Abs.*, 1932, 26, 565) were unable to estimate the yield of acrolein from glycerol by the usual aldehyde reactions owing to the instantaneous polymerization of acrolein. Formation of the bisulphite compound followed by determination of excess of bisulphite by titration with iodine (Ivanov's method) proved satisfactory.

<sup>132</sup> K. Noack, *British P.* 398,474, 1932; *Brit. Chem. Abs. B*, 1933, 955.

<sup>133</sup> C. Moureu and C. Dufraisse, *loc. cit.*

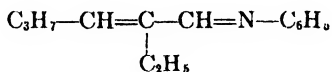
<sup>134</sup> T. Hanyu and T. Yanagibashi, *loc. cit.*

<sup>135</sup> L. Tampier and P. Gailliot, *loc. cit.*

<sup>136</sup> W. F. Darke and E. Lewis, *J. S. C. I.*, 1928, 47, 1085; *Ind. Eng. Chem., News Ed.*, 1925, 3, 5. Acrolein resins are said to have certain advantages over phenol-formaldehyde resins when they are made by reacting phenol and glycerol in the presence of a catalyst. The glycerol cannot be replaced by glycol. See G. S. Petrov and Y. A. Shmidt, *Plasticheskie Massy*, 1931 (1-2), 27; *Chem. Abs.*, 1932, 26, 3390.



anti-agers for rubber goods are obtained by condensation with aromatic bases. In one example, 39 parts of  $\alpha$ -ethyl- $\beta$ -propylacrolein dissolved in 60 volumes of benzene are heated with 21 parts of aniline in 25 volumes of benzene for 3-4 hours on the water bath under reflux. Benzene and water of reaction are driven off and the residue heated for several hours at 130°C. under 12 mm. The liquid residue is difficultly soluble in water and dilute acetic acid but easily soluble in organic solvents. The following is regarded as the probable chemical constitution:<sup>187</sup>



#### SATURATED ALIPHATIC ALDEHYDES

A very interesting study of polymerization of aldehydes under high pressures was made by Conant and Peterson<sup>188</sup> who prepared the polymers of normal and isobutyraldehyde, n-valeric aldehyde and n-heptaldehyde. From their experiments, it was concluded that a very small trace of a peroxide is essential for the change. A series of chain reactions in the liquid initiated from time to time by spontaneous decomposition of the peroxide are held to be responsible for polymerization. High pressure accelerates the reaction by arranging the molecules of aldehyde into a more compact mass in which longer reaction chains are developed on decomposition of a single molecule of peroxide. With increasing pressure and consequent diminution in the volume of liquid, the molecules begin to assume a definite orientation which is regarded as closely resembling that of the polymer itself. The fact that the polymer is more dense than the original material supports this contention. The formation of long reaction chains is probably encouraged by the spontaneous decomposition of peroxide molecules, each molecule in turn becoming activated by the decomposition energy of the peroxide and consequently joining up with an adjacent molecule. Pressure polymerization is thus visualized as a chain reaction in which a chain-like transmission of energy occurs and the increased rate of polymerization at high temperature is regarded as due to the increased frequency of peroxide decomposition and consequently the formation of more numerous reaction chains.

Freshly distilled acetaldehyde containing 5 per cent benzoyl peroxide polymerized to a hard solid under the usual conditions (see below) but failed to polymerize after heating out of contact with air for 115 hours. The presence of other liquids also diminished the rate of polymerization owing presumably to the hindrance which prevents the production of long reaction chains. On adding, for example, 10 per cent by volume of absolute ethyl alcohol to butyraldehyde which had absorbed considerable oxygen, a paste instead of a solid was obtained after 24 hours at 12,000 atmospheres; 15 per cent of alcohol completely prevented polymerization for 24 hours at 12,000 atmospheres while 28 per cent of n-butyric acid produced a similar effect.

As prepared at 12,000 atmospheres, the aldehyde polymers are hard transparent solids but at 4000-6000 atmospheres using benzoyl peroxide as the catalyst, the polymer is white. Completely polymerized butyraldehyde is insoluble in all common solvents and swells like rubber in benzene and toluene without dissolving. It does not possess any melting point, increase in temperature merely accelerating decomposition to n-butyraldehyde. Complete depolymerization is strongly

<sup>187</sup> W. Kropp, U. S. P. 1,845,755, Feb. 16, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2347.

<sup>188</sup> J. B. Conant and W. R. Peterson, *J.A.C.S.*, 1932, 54, 628.

catalyzed by aqueous acids or alkalies which bring about the change at atmospheric pressure in a few minutes at 25°C.

#### ALDEHYDE RESINS FROM PETROLEUM

James<sup>139</sup> describes a method for the production of resins by condensation of aldehyde-acids obtained by the partial oxidation of petroleum hydrocarbons. The aldehyde-acids were prepared by partial combustion of Pennsylvania gas oil and contained some unconverted hydrocarbons. Potash soaps were formed from the aldehyde fatty acids and separated from the reaction mixture. The soaps were then treated cold with a slight excess of 4 per cent hydrochloric acid and resinification took place immediately. The resinified acids were washed with water and dried. The color of the resin-acid mixture was light brown; it was brittle at room temperature, softened at 72°C. and melted at 100-120°C. The mixture of resin acids dissolved readily in benzene. The solvent evaporated rapidly, leaving a dark brown varnish coating which was tough and hard and possessed a gloss. Various other resins were obtained by change of conditions such as acid concentration and heat treatment and the use of a different crude oil. Another means of treatment of the partially oxidized hydrocarbons is with liquid sulphur dioxide to remove the unsaturated hydrocarbons. Subsequent boiling with 40 per cent aqueous formaldehyde yields a resin which may be used as a shellac substitute.<sup>140</sup>

#### HALOGENATED ALDEHYDES

In the preparation of 1,2-ethoxy-5-methoxy-3-pentyne by the action of chloroacetaldehyde on a mixture of ethyl magnesium bromide and methyl propargyl ether, the polymerization products of the aldehyde were resinified by potassium hydroxide.<sup>141</sup>

Bromoacetaldehyde may be obtained by the bromination of paraldehyde at low temperature. The compound is a lachrymator and very quickly becomes viscous and forms a white solid polymer. Acetaldehyde retards the polymerization.<sup>142</sup> Dichloroacetaldehyde assumes a dense form and finally becomes a white amorphous mass with an outward semblance of porcelain. On warming to 120°C., it is reconverted to the liquid.<sup>143</sup>  $\beta$ -Bromobutyraldehyde likewise polymerizes rapidly.<sup>144</sup> Benzylbromoacetaldehyde<sup>145</sup> is an unstable oil readily resinifying and polymerizing on standing; it yields a crystalline monohydrate.

Acraldehyde on halogenation in dilute aqueous solution gives the  $\alpha$ -mono-halogenated aldehydes. The  $\alpha$ -iodoacraldehyde (2-iodo-2-propenal-1) quickly becomes viscous.<sup>146</sup>

#### HYDROXY ALDEHYDES

Levene and Watti<sup>147</sup> prepared several  $\alpha$ -hydroxyaldehydes, namely; 2-hydroxypropanal-1, 2-hydroxybutanal-1 and 2-hydroxypentanal-1. These were mobile liquids when freshly distilled but polymerized rapidly at room temperature to

<sup>139</sup> J. H. James, U. S. P. 1,894,352, Jan. 17, 1932, to C. P. Byrnes; *Chem. Abs.*, 1933, 27, 2571. See Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934, 856, 857.

<sup>140</sup> R. B. Day, U. S. P. 1,933,716, Nov. 7, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1934, 28, 664. See Chapter 24 for use of other aldehydes.

<sup>141</sup> L. Lespieau, *Compt. rend.*, 1923, 176, 1068; *J.C.S.*, 1923, 124 (1), 531.

<sup>142</sup> A. Stepanov, N. Preobrazhenski and M. Shchukina, *Ber.*, 1925, 58, 1718; *Chem. Abs.*, 1926, 20, 242.

<sup>143</sup> J. Missenden, *Chem. Age. (London)*, 1922, 7, 78.

<sup>144</sup> L. Lespieau and R. L. Wakeman, *Compt. rend.*, 1931, 192, 1572.

<sup>145</sup> S. Danilov and E. Venus-Danilova, *Ber.*, 1930, 63, 2765; *J. Russ. Phys.-Chem. Soc.*, 1930, 62, 1097; *Chem. Abs.*, 1931, 25, 1819.

<sup>146</sup> A. Berlande, *Bull. soc. chim.*, 1925, (4) 37, 1385; *Brit. Chem. Abs. A*, 1926, 47.

<sup>147</sup> F. A. Levene and A. Watti, *J. Biol. Chem.*, 1931, 94, 353; *Chem. Abs.*, 1932, 26, 1900.

viscous liquids.  $\beta$ -Hydroxypropionaldehyde (3-hydroxy-1-propanal) polymerized at 90°C. under 18 mm. pressure.<sup>148</sup> d-4-Methylhexan-1-ol-6-al is a viscous amorphous substance.<sup>149</sup>

Gelation is recorded by Evans and Hass<sup>150</sup> as taking place under appropriate temperature conditions during the preparation of glyceric aldehyde acetal. The procedure consists of the oxidation of acrolein-acetal with potassium permanganate.

Dry hydrogen chloride when passed into isobutyraldehyde gives a heavy-bodied oil which resinifies with alkalis.<sup>151</sup> The condensation of isobutanol in the presence of potassium hydroxide produces an aldol which thickens on aging.<sup>152</sup>

### DIALDEHYDES

Glyoxal (CHO-CHO) when evaporated on a steam bath from an aqueous solution produces a water-containing amorphous solid. After drying in a vacuum at 110-120°C., the product polymerizes easily.<sup>153</sup> A yellowish-green vapor was noticed in the preparation of monomeric glyoxal; the color disappeared at room temperature, however, and a white mist was formed, an indication of rapid polymerization.<sup>154</sup>

Methyl glyoxal polymerized with the evolution of heat. Depolymerization could be effected by distillation.<sup>155</sup> Fischer and Taube<sup>156</sup> state that this liquid is green and that polymerization (as noticeable by a thickening of the liquid) sets in a few minutes after distillation. After a lapse of several hours, the product is a brittle, resin-like mass. Polymeric acetaldehyde on oxidation with aqueous nitric acid or analogous oxidizing agents leads to a glyoxal type of resin.<sup>157</sup>

Casein and other albuminous substances may be hardened by means of glyoxal or a condensation product. Electrical insulating and glass-like materials are said to be obtained.<sup>158</sup>

Mucono-dialdehyde (2,4-hexadien-1,6-dial) is very sensitive toward alkalis, the smallest trace of which turns the solution dark brown. Reduction of the aldehyde gives dark polymerization products, whereas oxidation, water-insoluble dark brown tars.<sup>159</sup> 1,10-Decandial,  $\text{OHC}-(\text{CH}_2)_8-\text{CHO}$ , also known as sebacic aldehyde, is a colorless oily liquid of pleasant odor. When freshly distilled and in the absence of a diluent, the aldehyde readily polymerizes to a glassy modification which does not give the typical aldehyde reactions.<sup>160</sup> Similarly, acetone-dihydroxysuccinic dialdehyde (acetone-1-tartaric dialdehyde) is a liquid which solidifies to a glassy mass.<sup>161</sup>

### BENZALDEHYDE AND OTHER AROMATIC ALDEHYDES

Benzaldehyde has somewhat less tendency to polymerize than formaldehyde and acetaldehyde. Its auto-reaction, that is, the formation of carbon-carbon

<sup>148</sup> A. V. Stepanov and M. Shchukina, *J. Russ. Phys.-Chem. Soc.*, 1926, 58, 840; *Chem. Abs.*, 1927, 21, 1094.

<sup>149</sup> B. Helferich and G. Sparmberg, *Ber.*, 1931, 64, 1151.

<sup>150</sup> W. L. Evans and H. B. Hass, *J.A.C.S.*, 1926, 48, 2703.

<sup>151</sup> S. Oeconomides, *Bull. soc. chim.*, 1881, (2) 35, 209; *Chem. Zentr.*, 1881, 723.

<sup>152</sup> V. Grignard and T. N. Iliesco, *Compt. rend.*, 1930, 190, 556.

<sup>153</sup> R. de Forcrand, *Bull. soc. chim.*, 1884, 41 (2), 242; *Chem. Zentr.*, 1884, 439.

<sup>154</sup> H. L. Riley and N. A. C. Friend, *J.C.S.*, 1932, 2345.

<sup>155</sup> H. L. Riley, J. H. Morley and N. A. C. Friend, *J.C.S.*, 1932, 1875.

<sup>156</sup> H. O. L. Fischer and C. Taube, *Ber.*, 1924, 57, 1502.

<sup>157</sup> M. Mugdau and J. Sixt, German P. 573,721, 1933, to Consort. für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 4253.

<sup>158</sup> K. Sponzel and O. Ernest, German P. 530,934, 1927, 485,189, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 869; 1930, 24, 930. British P. 279,863, 1926; *Chem. Abs.*, 1928, 22, 3025.

<sup>159</sup> F. G. Fischer and K. Löwenberg, *Ber.*, 1933, 66, 665.

<sup>160</sup> K. W. Rosenmund, F. Zetsche and F. Eulerlin, *Ber.*, 1922, 55, 609.

<sup>161</sup> H. O. L. Fischer and H. Appel, *Helv. Chim. Acta*, 1934, 17, 1374; *Chem. Abs.*, 1935, 29, 1781.

bonds such as the benzoin condensation, takes place only under the influence of catalysts or by the action of light. A compound similar to the paraldehyde of acetaldehyde, where carbon-oxygen-carbon bonds are formed, does not exist.<sup>123</sup>

It is not surprising therefore that the resinification of benzaldehyde is almost unknown. In alkaline solution the Cannizzaro reaction predominates. In acid solution, with sulphuric acid or with sulphuric-nitric acid, sulphonation and nitration take place. Ciamician and Silber,<sup>124</sup> however, obtained resins by the action of light on benzaldehyde. In one series of experiments they used pure benzaldehyde; in another they dissolved the aldehyde in alcohol. In both cases the samples were exposed to sunlight for three or four months at a time and resinous products were obtained. In one of a series of experiments 35 g. of benzaldehyde were utilized and after exposure the product was partially purified by steam distillation in order to remove unchanged benzaldehyde to yield 26 g. of solid resinous substance. When dissolved in ether, washed with sodium carbonate solution and evaporated to dryness, it was again taken up into solution, this time in benzene. Precipitation with petroleum ether gave a white pulverulent substance of melting point of 125-130°C. and which had the same elementary composition as benzaldehyde. In benzene the molecular formula was found to be represented by  $(C_7H_6O)_n$ .

The alcoholic-benzaldehyde solution, after exposure to light, was washed with benzene. This solution yielded both benzoin and hydrobenzoin on purification. The resin could be obtained from the benzene solution by the same means, precipitation with petroleum ether. This product has a molecular weight which corresponds to  $(C_{14}H_{12}O_2)_n$ , or four hydrobenzoin molecules.

When benzaldehyde (3 mols) is added to magnesium (1 at. wt.) and magnesium iodide in ether and benzene, and the resulting solution hydrolyzed with dilute acid, unchanged aldehyde, benzyl alcohol, benzoin and resinous material are obtained. If an excess of magnesium is used, benzyl alcohol and resinous material are the only products.<sup>125</sup> A mixture of benzaldehyde and acetic anhydride allowed to stand exposed to light reacts, yielding as one product a yellow resin.<sup>126</sup>

The reaction of benzaldehyde and metallic sodium forms in addition to other products a gummy residue part of which was identified as benzoin.<sup>126</sup> According to Kuhn and Ishikawa,<sup>127</sup> the attempts to condense benzaldehyde with crotonic acid resulted in the formation of resinous substances.

Benzaldehyde and dehydrocholic acid react in caustic soda solution to yield a solid soap-like mass which, on acidification with acetic acid, is obtained as an amorphous body that cannot be crystallized.<sup>128</sup> The substance sinters at 195°C. and on further heating gradually melts. The reaction of benzaldehyde, deoxybenzoin and aniline produces a resin.<sup>129</sup> Ciamician and Silber<sup>130</sup> obtained resinous products from the reaction of benzaldehyde, safrol and isosafrol under the influence of light.

Gentisaldehyde, m-hydroxybenzaldehyde, when treated with potassium persulphate in alkaline solution and strongly acidified furnishes a dark brown amorphous substance, which chars above 330°C. and is almost insoluble in all organic sol-

<sup>123</sup> In the Cannizzaro reaction with benzaldehyde a carbon-oxygen-carbon bond is formed; it is possible that the carbon-oxygen-carbon polymerization product is the intermediate of this reaction.

<sup>124</sup> G. Ciamician and P. Silber, *Ber.*, 1901, 34, 1538; 1903, 36, 1575.

<sup>125</sup> M. Gomberg and W. E. Bachmann, *J.A.C.S.*, 1930, 52, 4967.

<sup>126</sup> J. U. Nef, *Ann.*, 1897, 298, 282.

<sup>127</sup> F. F. Blicke, *J.A.C.S.*, 1924, 46, 2560.

<sup>128</sup> R. Kuhn and S. Ishikawa, *Ber.*, 1931, 64, 2347.

<sup>129</sup> W. Borsche and R. Frank, *Ber.*, 1924, 57, 1873.

<sup>130</sup> W. Dilthey and H. Steinborn, *J. prakt. Chem.*, 1932, (2) 133, 219; 1931, 130, 147.

<sup>131</sup> G. Ciamician and P. Silber, *Ber.*, 1909, 42, 1391.

vents except boiling glacial acetic acid.<sup>171</sup> Benzaldehyde cyanohydrin on standing yields resinous products which are probably polymers of benzoin.<sup>172</sup>

Raiford and Talbot,<sup>173</sup> in a study of the effect of substituents in certain condensations of benzaldehyde, treated 3,4-dimethoxybenzaldehyde and 5-bromo-3,4-dimethoxybenzaldehyde with potassium cyanide. In each case a viscous polymerization product was obtained as a residue, which was assumed to be a polymer of the benzoin of the corresponding substituted benzaldehyde. Secareanu,<sup>174</sup> in a study of the lability of nitro groups in the benzaldehyde nucleus, boiled solutions of o-nitrobenzaldehyde, 2,4-dinitrobenzaldehyde or 2,4,6-trinitrobenzaldehyde with benzyl chloride. Hydrogen chloride and nitrogen oxides were evolved and resinous products obtained. Anisaldehyde and dehydrocholic acid yield a dark yellow resin.<sup>175</sup> Benzylidenepyruvic acid (obtained by condensation of benzaldehyde with pyruvic acid in the presence of hydrochloric acid), when dried in vacuum at 25°C., becomes an amorphous solid, which softens at 80°C. and on further heating decomposes.<sup>176</sup> Ciamician and Silber<sup>177</sup> found a mixture of anisaldehyde, benzoin, benzophenone and formic acid to become partially resinified on exposure to light. Benzil dissolved in ethyl alcohol also yielded a resin when similarly treated.

The action of a mixture of acetic acid and acetic anhydride containing sulphuric acid on piperonal and vanillin produces dark-colored condensation products.<sup>178</sup> 4,6-Dinitro-m-xylene, when reacted with aldehydes in the presence of sodium alcoholate, forms resinous substances.<sup>179</sup> Resinification also occurs when p-dimethylaminobenzaldehyde and cinnamaldehyde, or its bromine derivative, are condensed with 4,6-dinitro-m-xylene. König, Schramek and Rösch<sup>180</sup> report the copious formation of acetaldehyde resin when p-dimethylaminobenzaldehyde reacted with paraldehyde or acetaldehyde in the presence of concentrated sulphuric acid. Resins are obtained from benzoylacetone with pyridine as the condensing agent, in benzene-ligroin solution, with the following aldehydes: anisaldehyde, piperonal and m-nitrobenzaldehyde. Reaction of aniline, formaldehyde and desoxybenzoin yields a resin.<sup>181</sup> Phenyl-o-anisylacetaldehyde, phenyl-m-anisylacetaldehyde and 2,4'-dimethoxydiphenylacetaldehyde are easily resinified on distillation even under reduced pressure.<sup>182</sup> When carrying out the reaction between isovaleric aldehyde and salicylic amide, it is necessary to keep the temperature below 70°C. otherwise the aldehyde is largely resinified.<sup>183</sup> Several attempts were made by Curtis and co-workers<sup>184</sup> to condense isovaleric aldehyde with cyanoacetamide, but only a small amount of sticky solid was obtained.

Two hundred grams of cinnamaldehyde and 50 g. of potassium hydroxide in 1700 cc. of water were heated 8 hours at 100°C.; after steam distillation of the residue 120 g. of resin were found.<sup>184a</sup> Formaldehyde reacts with cinnamic aldehyde in the presence of calcium or barium hydrates, at temperatures above 50°C., to yield a resin.<sup>186</sup> The action of chloroform and sodium hydroxide on salicylic acid

<sup>171</sup> H. H. Hodgson and H. G. Beard, *J.C.S.*, 1927, 2339

<sup>172</sup> G. Bunning, *Arch. Pharm.*, 1928, 266, 231.

<sup>173</sup> L. C. Raiford and W. F. Talbot, *J.A.C.S.*, 1932, 54, 1092.

<sup>174</sup> S. Secareanu, *Ber.*, 1931, 64, 837.

<sup>175</sup> W. Borsche and K. Frank, *Ber.*, 1924, 57, 1373.

<sup>176</sup> L. Musajo, *Gazz. chim. ital.*, 1932, 62, 901; *Brit. Chem. Abs. A*, 1933, 64.

<sup>177</sup> G. Ciamician and P. Silber, *loc. cit.*

<sup>178</sup> H. Friese, *Ber.*, 1930, 63, 1902.

<sup>179</sup> P. Ruggli, A. Zimmermann and R. Thonvay, *Helv. Chim. Acta*, 1931, 14, 1250; *Chem. Abs.*, 1932, 26, 2177.

<sup>180</sup> W. König, W. Schramek and G. Rösch, *Ber.*, 1928, 61, 2074.

<sup>181</sup> W. Dilthey and H. Steinborn, *J. prakt. Chem.*, 1932, (2) 133, 219.

<sup>182</sup> J. Levy and R. Perrot, *Bull. soc. chim.*, 1931, (4) 49, 1780; *Brit. Chem. Abs. A*, 1932, 390.

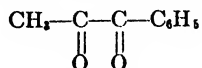
<sup>183</sup> V. Moucka and C. Rögl, *Ber.*, 1928, 59, 758.

<sup>184</sup> R. H. Curtis and C. N. E. Day and L. G. Kinnins, *J.C.S.*, 1923, 123, 3131.

<sup>184a</sup> M. J. Viard, *Parfums de France*, 1924, 15, 103; *Chem. Abs.*, 1924, 18, 2335.

<sup>185</sup> C. M. van Marle and B. Tollens, *Ber.*, 1903, 36, 1347.

is accompanied by the production of some tarry matter.<sup>186</sup> Salicylaldehyde forms a resinous substance when warmed with aniline and methyl phenyl diketone



in alcohol. In the making of protocatechuic aldehyde from catechol, chloroform and caustic soda, a black resin is formed.<sup>187</sup> The preparation of tetrahydronaphthalene aldehyde takes place with much resinification.<sup>188</sup> Piperonylmethylpropylene glycol undergoes resinification with concentrated sulphuric acid (sp. gr. 1.84) even at  $-20^\circ\text{C}$ .<sup>189</sup> One hundred grams of cinnamaldehyde and 100 g. of amylene were exposed to sunlight in a glass tube for 3 months by Alujevich.<sup>190</sup> The product is described as a tarry residue. 1,3-Diphenylpropene ( $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$ ) on oxidation with permanganate yields a glycol which resinifies on the addition of ammoniacal silver solution. This is ascribed by Stoermer and Thier<sup>191</sup> to the formation of 1,2-diphenylpropionaldehyde.<sup>192</sup> 7-Phenyl-2,4,6-heptatrienal-1 ( $\text{C}_6\text{H}_5-(\text{CH}=\text{CH})_3-\text{CHO}$ ) reacts with p-anisidine and with p-phenetidine to form crystalline derivatives, which on treatment with ammoniacal silver nitrate, yield acids which resinify quickly.<sup>193</sup> The phenylhydrazone of  $\alpha$ -bromocinnamaldehyde is resinified by hot acetic acid.<sup>194</sup> The phenylhydrazone of 2,4,6-octatrienal-1 ( $\text{CH}_3-(\text{CH}=\text{CH})_3-\text{CHO}$ ) polymerizes in an inert atmosphere in a few hours.<sup>195</sup>

Hodgson and Jenkinson<sup>196</sup> conducted the Reimer-Tiemann reaction on a solution of resorcinol monomethyl ether. A considerable amount of resinous material was formed. On shaking a cold saturated solution of benzoin in pyridine with solid sodium cyanide, Lachmann<sup>197</sup> observed gradual gel formation. Two grams of finely crystallized sodium cyanide were added to a cold solution of 10 g. of benzoin in 60 cc. of pyridine dried over sodium and the mixture gently shaken. Gel formation took place slowly and the product, upon standing overnight, did not dissolve when warmed to  $35-40^\circ\text{C}$ . It is considered to be an addition product of benzoin and sodium cyanide, but the benzoin content was subject to wide variations, analysis revealing figures ranging from 23-43 per cent. An equimolecular addition product would call for a benzoin content of 81 per cent. The gel is readily hydrolyzed by water or ethyl alcohol. Potassium cyanide fails to give gel formation.

$\alpha$ -Naphthaldehyde when heated with succinic anhydride and anhydrous sodium acetate above  $122^\circ\text{C}$ . results in the formation of tar which renders difficult the purification of  $\alpha$ -naphthylparaconic acid.<sup>198</sup> The semicarbazone of dicyclohexylacetaldehyde was resinified by heating with 55 per cent sulphuric acid.<sup>199</sup>  $\alpha$ -Campholenic aldehyde,

<sup>186</sup> E. J. Wayne and J. B. Cohen, *J.C.S.*, 1922, 121, 1022.

<sup>187</sup> F. Tiemann and P. Koppe, *Ber.*, 1881, 14, 2015.

<sup>188</sup> H. Weil and H. Ostermeier, *Ber.*, 1921, 54B, 3217.

<sup>189</sup> M. Tiffeneau and J. Levy, *Bull. soc. chim.*, 1931, (4) 49, 1738; *Brit. Chem. Abs. A*, 1932, 390.

<sup>190</sup> N. Alujevich, *Atti. accad. Lincei*, 1923, 32 (2), 292; *Gazz. chim. ital.*, 1924, 54, 191; *Chem. Abs.*, 1924, 18, 3184.

<sup>191</sup> R. Stoermer and C. Thier, *Ber.*, 1925, 58, 2607.

<sup>192</sup> Similar transformations involving phenyl groups have been described by M. Tiffeneau, *Compt. rend.*, 1906, 142, 1537; *J.C.S.*, 1906, 90 (1), 662; M. Tiffeneau and Dorlencourt, *Compt. rend.*, 1906, 143, 126; *Chem. Zentr.*, 1906, 2, 670; M. Tiffeneau and Dorlencourt, *Ann. chim. phys.*, 1909, (8) 16, 237; *Chem. Zentr.*, 1909, 1, 1335.

<sup>193</sup> D. Vorländer, E. Fischer and K. Kunze, *Ber.*, 1925, 58, 1284.

<sup>194</sup> K. U. Auwers and B. Ottens, *Ber.*, 1925, 58, 2060.

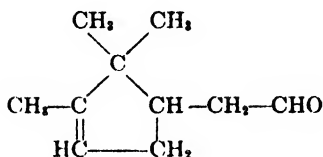
<sup>195</sup> R. Kuhn and M. Hoffer, *Ber.*, 1931, 64, 1977.

<sup>196</sup> H. H. Hodgson and T. A. Jenkinson, *J.C.S.*, 1929, 1641.

<sup>197</sup> A. Lachmann, *J.A.C.S.*, 1924, 46, 708.

<sup>198</sup> J. B. Shoosmith and A. Guthrie, *J.C.S.*, 1928, 2332.

<sup>199</sup> E. Venus-Danilova, *Ber.*, 1928, 61, 1954.



is easily resinified by alkalis.<sup>300</sup>  $\alpha$ -Homoheliotropin<sup>301</sup> is a light yellow oil which resinifies easily by the action of heat, air and alkali.

Reduction of 2-nitro-2-(hydroxymethyl)-1,4-butanediolone with sodium amalgam in aluminum sulphate solution yielded the hydroxylamine derivative as a clear brownish-yellow uncrystallizable gum.<sup>302</sup>

#### PREPARATION AND PROPERTIES OF FORMALDEHYDE ✓

Commercial "formalin," a 40 per cent by volume (37 per cent by weight) aqueous solution of formaldehyde, is generally prepared by the oxidation of methyl alcohol. Methyl alcohol vapor mixed with appropriate quantity of air is carefully led over a contact catalyst and the resulting product condensed. The excess of methyl alcohol is removed by distillation.

Formaldehyde is a gas which can be condensed to a liquid boiling at  $-21^\circ\text{C}.$ ; the liquid aldehyde polymerizes at its boiling point. Evaporation of a solution of formaldehyde results in the production of paraform, a polymer of formaldehyde.

The commercial formalin contains not only the simple formaldehyde but also polymeric forms; the latter being insoluble in water, tend to precipitate. To maintain the polymers in solution, methyl alcohol is not entirely removed and a definite quantity, from 6-14 per cent, is allowed to remain. Due to temperature differences between summer and winter, the methyl alcohol content is varied slightly to prevent any precipitation occurring. In addition to the methyl alcohol, there are small amounts of formic acid and also some methylal which arises from the reaction between methyl alcohol and formaldehyde.

One of the largest sources of methyl alcohol for the manufacture of formaldehyde has been the wood distilleries. With the advent of synthetic methanol, the natural source has been curtailed. The greatly increased production of gaseous hydrocarbons (coal gas, natural gas, cracking gas) has led to many investigations to use these substances as raw materials for the preparation of formaldehyde by partial oxidation.<sup>303</sup> Natural gas or gases from the distillation of coal, petroleum or shale when mixed with air, oxygen or carbon dioxide and allowed to react at  $425\text{--}485^\circ\text{C}.$  with a catalyst (platinum, palladium, gold, silver, copper, chromium, manganese, iron, nickel or their oxides), gave rise to alcohols and aldehydes. By appropriate variation of conditions and catalysts, it was possible to carry out the reaction in stages; methane could be oxidized to methanol and in another step to formaldehyde.<sup>304</sup>

#### REACTIONS OF FORMALDEHYDE

Formaldehyde can combine with itself to form compounds of higher molecular weight in two general reactions. The first of these forms a carbon-carbon bond

<sup>300</sup> P. Lipp and F. Lausberg, *Ann.*, 1924, 436, 274; *Chem. Abs.*, 1924, 18, 1837. For constitution of  $\alpha$ -campholenaldehyde see G. Ciamician and P. Silber, *Ber.*, 1910, 43, 1340; *Chem. Abs.*, 1910, 4, 2481.

<sup>301</sup> S. Nagai, *J. Chem. Ind., Japan*, 1922, 25, 1409; *J.S.C.I.*, 1923, 42, 291A.

<sup>302</sup> W. Charlton and J. Kenner, *J.C.S.*, 1932, 754.

<sup>303</sup> For further review, see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

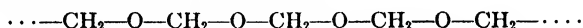
<sup>304</sup> J. C. Walker, British P. 290,613, 1927 and 295,856, 1927, to Empire Gas and Fuel Co.; *Chem. Abs.*, 1929, 23, 846, 2186. Canadian P. 300,567, 1930; *Chem. Abs.*, 1930, 24, 3516.

and produces a carbohydrate type of molecule; the second proceeds with the elimination of water from molecules of methylene glycol,  $\text{H}_2\text{C}(\text{OH})_2$ , or polymethylene glycols,  $\text{HO}-(\text{CH}_2\text{O})_n-\text{CH}_2\text{OH}$ .<sup>205</sup>

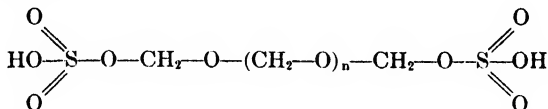
The formation of carbohydrates, first observed by Butlerow,<sup>206</sup> has been studied by Loew,<sup>207</sup> Fischer,<sup>208</sup> H. and A. Euler,<sup>209</sup> Schmalfluss<sup>210</sup> and others. Various condensing agents have been used: calcium hydroxide,<sup>206, 207</sup> magnesium hydroxide,<sup>210</sup> lead oxide,<sup>207</sup> calcium carbonate<sup>209</sup> and the acetates of lead, calcium and magnesium,<sup>207</sup> both at room temperature and at 100°C. Products of the general formula of  $(\text{H}_2\text{CO})_n$  are obtained, along with both acetic acid and methyl alcohol, that is, the Cannizzaro-reaction products of formaldehyde. Further polymerization of the sugar results in the formation of a brown dye but no resinous products.

The products of the second type of polymerization in which carbon-oxygen-carbon bonds are formed are usually white powders which in contrast to the carbohydrate type are rather easily depolymerized by sodium sulphite, alkali or water. Water is needed to promote this second type of polymerization.<sup>211</sup>

Numerous polymers of formaldehyde are known and they have been studied extensively especially by Staudinger<sup>212</sup> in an attempt to elucidate the structure of cellulose.<sup>213</sup> On the basis of the structures of other linear polymers<sup>214</sup> the formula assigned to the formaldehyde polymers<sup>215</sup> is



Paraform<sup>216</sup> is a mixture of polymer homologs where the number of monomeric units varies from 6 to 50 and is ordinarily prepared by the simple evaporation of aqueous formaldehyde solutions.<sup>217</sup>  $\alpha$ -Polyoxymethylene<sup>218</sup> is also a mixture of polymers but the number of monomer units is 100 or greater; it is formed by the action of dehydrating agents upon formaldehyde.  $\beta$ -Polyoxymethylene<sup>219</sup> is obtained by using a higher concentration of sulphuric acid than is necessary to form the  $\alpha$ -compound. The constitution of this polymer is not known exactly; it is similar in most of its physical properties to the  $\alpha$ -derivative and may be a sulphuric-acid derivative of it.



<sup>205</sup> For a review of formaldehyde with respect to industrial uses and occurrence, see J. Coulouma, *Rev. gen. mat. plastiques*, 1928, 4, 3, 73, 152, 263, 329; *Chem. Abs.*, 1928, 22, 4105.

<sup>206</sup> A. Butlerow, *Compt. rend.*, 1861, 53, 145.

<sup>207</sup> O. Loew, *J. prakt. Chem.*, 1886, (2), 33, 321; *Ber.*, 1888, 21, 272; 1889, 22, 470; 1906, 39, 1562.

<sup>208</sup> E. Fischer, *Ber.*, 1883, 21, 988.

<sup>209</sup> H. and A. Euler, *Ber.*, 1906, 39, 45.

<sup>210</sup> H. Schmalfluss and K. Kalle, *Ber.*, 1924, 57, 2102; *Chem. Abs.*, 1925, 19, 1403.

<sup>211</sup> F. Walker, *J.A.C.S.*, 1933, 55, 2821.

<sup>212</sup> H. Staudinger, "Die hochmolekularen organischen Verbindungen," Julius Springer, Berlin, 1932.

<sup>213</sup> See H. Staudinger and K. Hess, *Ber.*, 1934, 67, 475; *Chem. Abs.*, 1934, 28, 3059.

<sup>214</sup> See Chapter 4.

<sup>215</sup> H. Staudinger and M. Lüthy, *Helv. Chim. Acta*, 1925, 8, 41, 65, 67; *Chem. Abs.*, 19, 1245, 1246.

<sup>216</sup> H. Staudinger, R. Signer, H. Johnner, M. Lüthy, W. Kern, D. Russidas and O. Schweitzer, *Ann.*, 1929, 474, 241; *Chem. Abs.*, 1930, 24, 3754. See F. Walker, *Ind. Eng. Chem.*, 1931, 23, 1220.

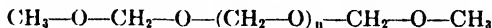
<sup>217</sup> Polyoxymethylenes can be prepared in the presence of alkaline catalysts (ammonia, ammonium salts, hexamethylenetetramine, amines, ethanol amines, urea, pyrones and quaternary ammonium bases). See G. Pirlet, French P. 765,540, 1934; *Chem. Abs.*, 1934, 28, 6724. Cf. the inclusion of a protective colloid (egg albumin) L. Nasch, British P. 420,998, 1933; *Brit. Chem. Abs. B*, 1935, 139. E. Riets (U. S. P. 1,213,261, Jan. 23, 1917, to Synthetic Patents Co.; *Chem. Abs.*, 1917, 11, 872) obtained a product for therapeutic purposes from cholic acid and paraformaldehyde.

<sup>218</sup> H. Staudinger, R. Signer, H. Johnner, M. Lüthy, W. Kern, D. Russidas and O. Schweitzer, *Ann.*, 1929, 474, 241; *Chem. Abs.*, 1930, 24, 3754. See F. Walker, *Ind. Eng. Chem.*, 1931, 23, 1220. F. Pollak, U. S. P. 1,280,600, June 17, 1917; *Chem. Abs.*, 1917, 11, 2266.

<sup>219</sup> H. Staudinger, et. al., *Ann.*, 1929, 474, 245.



$\gamma$ - and  $\delta$ -Polyoxymethylenes<sup>220</sup> are not true polymers of formaldehyde.  $\gamma$ -Polyoxymethylene appears to be dimethyl ether of the higher polyoxymethylene glycols



It is precipitated along with  $\alpha$ -polyoxymethylene when concentrated sulphuric acid is added to a formaldehyde solution containing methyl alcohol.  $\delta$ -Polyoxymethylene is formed when the  $\gamma$ -polymer is heated with water.

Trioxo-<sup>221</sup> and tetraoxomethylene, made up of three and four molecules of formaldehyde, respectively, have been isolated.  $\epsilon$ -Polyoxymethylene,<sup>222</sup> a white amorphous non-crystalline paper-like substance, is left behind when  $\alpha$ -trioxomethylene is sublimed. Its molecular species is unknown.

It is to be emphasized that all the previously mentioned oxymethylene polymers with the exception of  $\epsilon$ -polyoxymethylene are crystalline substances and while they may be prepared having the consistency of a grease,<sup>223</sup> they are never resinous. Staudinger and Kern<sup>224</sup> have prepared a polymer of formaldehyde which has the properties of a resin (see Fig. 84). This substance is called eu-polyoxymethylene



Fig. 84.—Glass, Film and Fiber Forms of Polyoxymethylene Prepared by H. Staudinger

and is formed by the spontaneous polymerization of pure monomolecular liquid formaldehyde at low temperatures.

The polymerization, when carried out at  $-80^{\circ}\text{C}.$ , especially in oxygen, leads to a clear transparent somewhat brittle glass; at  $-20^{\circ}\text{C}.$  an opaque solid is formed. The eu-polymers formed at lower temperatures ( $-80^{\circ}\text{C}.$ ) become plastic and elastic when heated to  $160\text{--}200^{\circ}\text{C}.$  In this condition they are very viscous and tenacious and can be formed and kneaded. These properties distinguish them very sharply from  $\alpha$ - or  $\beta$ -polyoxymethylene. The polymers formed at  $-20^{\circ}$  can be drawn out into threads 1 meter or more in length and may be pressed into films. The threads can be stretched to about 10 per cent of their length. Films may also be produced by distillation of monomolecular formaldehyde in vacuum, the receiver being at  $-80^{\circ}\text{C}.$  If cooled with liquid air solid monomolecular formaldehyde is produced which shows no tendency to polymerize. The specific gravity of the glass-clear polymer at  $20^{\circ}\text{C}.$  is 1.407. The products show no defi-

<sup>220</sup> H. Staudinger, et. al., *Ann.*, 1929, 474, 218, 232.

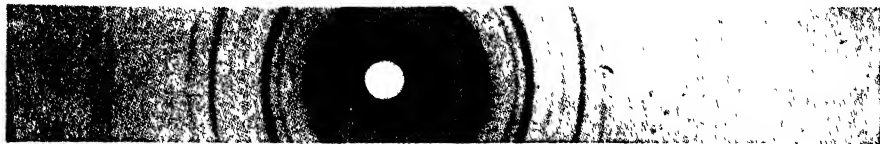
<sup>221</sup> F. Auerbach and H. Barschall, *Arb.kaus.Gesundh.*, 1905, 22, 584; *Chem. Zentr.*, 1905, 2, 1081. D. L. Hammick and A. R. Boeree, *J.C.S.*, 1922, 121, 2738. H. Staudinger and M. Lüthy, *Helv. Chim. Acta*, 1925, 8, 65. Trioxymethylene changes in *vacuo* to what appears to be a chain polymer. The reaction occurs at the solid-gas interface and may be due to a change in molecular configuration when the solid trioxymethylene vaporizes. Neither molten trioxymethylene or tetraoxymethylene undergoes the reaction. See H. W. Kohlshütter and L. Sprenger, *Z. physik. Chem.*, 1932, B16, 284; *Chem. Abs.*, 1932, 26, 3480.

<sup>222</sup> D. L. Hammick and A. R. Boeree, *loc. cit.*

<sup>223</sup> British P. 260,908, 1925, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1927, 59.

<sup>224</sup> H. Staudinger, "Die hochmolekularen organischen Verbindungen," Berlin, 1932. W. Kern, *Kolloid-Z.*, 1932, 61, 308; *Brit. Chem. Abs.* A, 1933, 14.

nite melting point; at high temperatures they sinter with the evolution of formaldehyde.



Courtesy Julius Springer, Berlin

FIG. 84a.—X-ray Diagram of High-molecular Polyoxymethylene Dimethylether.\*  
(H. Staudinger)

\* A discussion of x-ray studies is found in Chapter 4.

Staudinger<sup>226</sup> considers the difference between eu-polyoxymethylene and the oxymethylene-polymers, obtained from aqueous solution, to be due to the much



Courtesy Julius Springer, Berlin

FIG. 84b.—Diagram of  $\gamma$ -Polyoxymethylene. (H. Staudinger)

larger molecular weight of the eu-polymer, and that this difference is caused by the different reaction mechanism in the two cases. Eu-polyoxymethylene forma-



FIG. 84c.



FIG. 84d

Courtesy Julius Springer, Berlin

FIG. 84c.—Diagram of Polyoxymethylene Dihydrate Gel Immediately after Formation.  
(H. Staudinger)

FIG. 84d.—Gel of Fig. 84c after Two Days. (H. Staudinger)

tion he says is a chain reaction, while the solution reaction is simply a condensation of methylene glycols. Sauter<sup>228</sup> on the other hand measured the molecular diffraction pattern of eu-polyoxymethylene and also  $\beta$ - and  $\delta$ -polyoxymethylene and

<sup>226</sup> H. Staudinger, *loc. cit.* H. Staudinger and W. Kern, *Ber.*, 1933, 66, 1893.

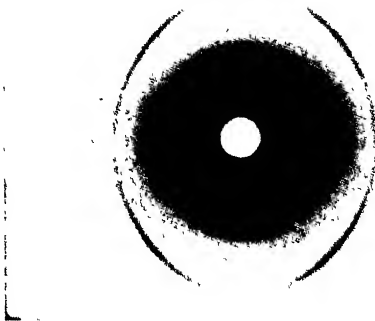
<sup>228</sup> E. Sauter, *Zeits. physik. Chem.*, 1933, B21, 161, 186; *Chem. Abs.*, 1933, 27, 3867.

came to the conclusion that the eu-polyoxymethylene has a different molecular structure. Walker<sup>227</sup> says that his powder-like polymer dissolved in alkali but does not mention whether it reverted to monomolecular formaldehyde or not.

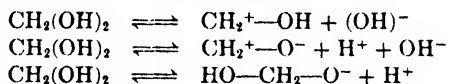
The study of the magnetic susceptibilities<sup>228</sup> of the four polyoxymethylenes indicates that these derivatives are mixtures of substances having the general formula,  $\text{CH}_2-(\text{O}-\text{CH}_2)_n-\text{O}-\text{CHO}$ . Moreover, the kinetics of the polymerization reactions of aqueous solutions of formaldehyde denote that the oxygen linkings in polymeric formaldehyde are the same as in amides, esters and semi-acetals and that the mechanism of polymerization and depolymerization of formaldehyde in

FIG. 84e—X-Ray Diagram of a eu-Polyoxymethylene Fiber. (H. Staudinger)

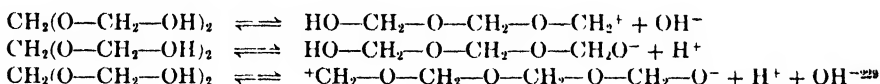
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water is similar to that of formation and rupture of these linkages. In dilute solution the following equilibria are assumed:



whereas in concentrated solution:



On pyrex-glass the polymerization of formaldehyde is unimolecular at high pressures.<sup>230</sup>

#### REACTIONS OF FORMALDEHYDE WITH CERTAIN OTHER SUBSTANCES

Water-insoluble products are formed by treating water-soluble cellulose alkyl ethers with aldehydes in the presence of catalysts.<sup>231</sup> For example, methylcellulose foil is treated with formaldehyde in potassium hydroxide at 95°C. It is not stated whether the products are resinous.

Bornyl and isobornyl chlorides condense with formaldehyde in the presence of ferric chloride and form black resinous products which are soluble in benzene, ether

<sup>227</sup> F. Walker, *loc. cit*

<sup>228</sup> W. Good, *J. Roy. Tech. Coll. Glasgow*, 1931, 2, 401; *Brit. Chem. Abs. A*, 1931, 411.

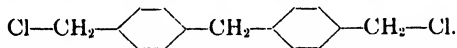
<sup>229</sup> M. Wadano, C. Trogus and K. Hess, *Ber.*, 1934, 67, 174; *Brit. Chem. Abs. A*, 1934, 493. For the acidic nature of aqueous formaldehyde solution see M. Wadano, *Ber.*, 1934, 67, 191; *Brit. Chem. Abs. A*, 1934, 393.

<sup>230</sup> R. Spence, *J.C.S.*, 1933, 1193.

<sup>231</sup> K. Sponse and G. Balle, German P. 538,686, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2316.

and gasoline.<sup>233</sup> Hydrochloric acid is evolved in the process. When the condensation is carried out in sulphuric acid, however, the resinous products are found to be soluble in benzene but insoluble in ether and gasoline.

When sulphuric acid and acetic acid are slowly added to benzoyl chloride and trioxymethylene, a derivative is formed of the structure



Treatment with silver nitrate yields the dinitrate, which with alkali gives rise to a viscous polymer,  $(\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_4-\text{CH}_2\text{OH})_n$ .<sup>234</sup> The condensation of anethol (p-propenylanisol) with formaldehyde gave the methylene ether of p-methoxyphenylbutyl glycol which resinified when attempts were made to saponify it.<sup>235</sup>

Condensation of 1-borneol with formaldehyde yields resinous products if the reaction is carried out in the cold and in the presence of concentrated sulphuric acid.<sup>235</sup> An oil is obtained if the condensation is carried out with heating and concentrated acids. The oil, when distilled in the presence of sulphuric acid, yields pitches which are soluble in benzene and might be utilized as lacquers.

Solutions of paraformaldehyde when heated in alcohol with zinc oxide or alumina give rise to a formaldehyde polymer which is soluble in organic solvents and which may be used for production of formaldehyde-phenol resins.<sup>236</sup> The acetal prepared from ethyl alcohol and formaldehyde when treated with an excess of magnesium oxide yielded a starch-like substance.<sup>237</sup>

Although the reaction of formaldehyde with tri- and tetra-chloroethylene in the presence of concentrated sulphuric acid produces identifiable products, the reaction of this aldehyde with dichloroethylene,  $\text{H}_2\text{C}=\text{CCl}_2$ , gives only resinous substances.<sup>238</sup>

The hardening of lac from "*Rhus vernicifera*"<sup>239</sup> can be accelerated by pre-boiling in water which may contain a condensing agent such as formaldehyde.<sup>240</sup>

<sup>232</sup> S. N. Ushakov and A. D. Sokolov, *J. Appl. Chem., Russia*, 1930, 3, 47; *Brit. Chem. Abs. B*, 1930, 1120.

<sup>233</sup> E. Connerade, *Bull. soc. chim. Belg.*, 1932, 41, 337; *Chem. Abs.*, 1933, 27, 716.

<sup>234</sup> H. J. Prins, *Proc. Acad. Sci. Amsterdam*, 1919, 22, 51; *Chem. Abs.*, 1920, 14, 1662.

<sup>235</sup> S. N. Ushakov and A. D. Sokolov, *J. Appl. Chem., Russia*, 1930, 3, 47; *Brit. Chem. Abs. B*, 1930, 1120.

<sup>236</sup> R. Gebauer, German P. 434,830, 1923, to Chem. Fabr. von Heyden A.-G.; *Brit. Chem. Abs. B*, 1927, 348.

<sup>237</sup> A. Barreto, *Rev. chim. ind. (Rio de Janeiro)*, 1933, 2, 455; *Chem. Abs.*, 1934, 28, 3384. See Carleton Ellis, U. S. P. 1,903,809, Apr. 18, 1933, to Ellis-Foster Co., *Brit. Chem. Abs. B*, 1933, 1021. Carleton Ellis, U. S. P. 1,691,271, Nov. 13, 1928, *Brit. Chem. Abs. B*, 1929, 566. H. M. Weber, U. S. P. 1,692,524, Nov. 26, 1928, to Ellis-Foster Co.; *Brit. Chem. Abs. B*, 1929, 256.

<sup>238</sup> H. J. Prins, *Rec. trav. chim.*, 1932, 51, 469; *Brit. Chem. Abs. A*, 1932, 721.

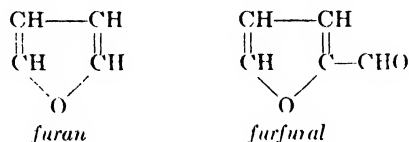
<sup>239</sup> Japan lac is a lactiferous secretion from "*Rhus vernicifera*." For constitution see R. Majima, *Ber.*, 1922, 55, 191. and previous papers. See also Chapter 2, page 25.

<sup>240</sup> X. Winter, *British P.* 390,377, 1932; *Brit. Chem. Abs. B*, 1933, 479.

## Chapter 24

### Furfural Resins

Furfural (fural, furfurol, furfuraldehyde) is a heterocyclic aldehyde of the furan series



that exhibits many resin-forming reactions. Döbereiner<sup>1</sup> first obtained this aldehyde as a by-product in the preparation of formic acid by the action of sulphuric acid and manganese dioxide on sugar.<sup>2</sup> Commercially, furfural is obtained by acid hydrolysis of pentosans occurring naturally in vegetable materials such as bran, corncobs, oat hulls, rice hulls and kapok.<sup>3</sup> Oat hulls are employed principally in the large-scale production of furfural (see Fig. 85). The hulls are moistened with dilute sulphuric acid and the mixture heated to 145°C. under pressure. Simultaneously steam is passed through the hot mass, and furfural is separated from the condensed vapors by distillation.<sup>4</sup>

The pure compound is a colorless liquid (sp. gr. 1.16) which boils at 161.7°C., freezes at -38°C. and becomes brown on exposure to air. It dissolves in water, alcohol and ether.<sup>5</sup> Because of its heterocyclic structure (i.e., the presence of the furan ring) furfural exhibits chemical properties markedly different from those

<sup>1</sup> J. W. Döbereiner, *Ann.*, 1832, 3, 141.

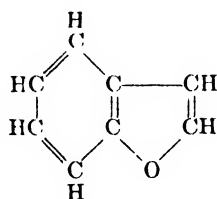
<sup>2</sup> For work of other early investigators, see L. V. Babo, *Ann.*, 1853, 85, 100. A. Cahours, *Ann.*, 1849, 69, 82. Emmet, *J. prakt. Chem.*, 1837, 12, 120. Gudkow, *Ber.*, 1870, 3, 425. For reviews on properties and preparation, see F. Hardy, *Trop. Agr.*, 1924, 1, 158; *Chem. Abs.*, 1925, 19, 76. Van Os, *Chem. Weekblad*, 1925, 22. A. J. Hammett, *J.S.C.I.*, 1933, 52, 608.

<sup>3</sup> Other methods of preparing furfural from these materials are described by: G. Mains, *Chem. Met. Eng.*, 1922, 26, 779, 841. V. V. Chelintzev and A. F. Vorob'ev, *J. Chem. (Moscow)*, 1933, 2, 27; *Chem. Abs.*, 1933, 27, 4281. F. B. LaForge, *Ind. Eng. Chem.*, 1923, 15, 499. G. Mains and F. B. LaForge, *Ind. Eng. Chem.*, 1924, 16, 356; 1923, 15, 823, 1057. K. P. Monroe, *Ind. Eng. Chem.*, 1921, 13, 133. K. P. Monroe, U. S. P. 1,357,467, Nov. 2, 1920; *J.S.C.I.*, 1921, 40, 27A. F. B. LaForge, C. W. Tooke, G. Mains and W. Clarke, *British P.* 207,116, 1923; *J.S.C.I.*, 1924, 43, 76B. O. R. Sweeney, *Iowa State Coll. Eng. Expt. Sta. Bull.*, 1924, 73, 7; *Chem. Abs.*, 1925, 19, 3353. E. L. Hunt and D. R. Morrison, *J.C.S.*, 1923, 123, 3226. H. Utsuka, *Rep. Osaka, Ind. Res. Lab.*, 1925, 5 (16) 1. *Chem. Abs.*, 1925, 19, 2336. O. D. Lucas, *British P.* 298,800, 1926, to Vickers, Ltd.; *Chem. Abs.*, 1929, 23, 3098. A. Classen, *French P.* 727,335, 1931. *Chem. Abs.*, 1932, 26, 5106. F. W. Klingstedt, *Zellulose u. Papier*, 1928, 8, 471; *Brit. Chem. Abs. A.*, 1928, 992. E. Heuser and W. Schott, *Cellulosechemie*, 1923, 4, 85; *Chem. Abs.*, 1924, 18, 391. A. E. Arbutov and B. P. Lukovkin, *J. Appl. Chem. Russ.*, 1934, 7, 550; *Brit. Chem. Abs. B.*, 1935, 56. D. I. Miris and I. B. Dranovskii, *Lesokhimbicheskaya Prom.*, 1933, 2 (6), 23; *Chem. Abs.*, 1935, 29, 1813. B. S. Groth and G. H. Blomqvist, *German P.* 604,018, 1934; *Chem. Abs.*, 1935, 29, 820. U. S. P. 1,960,812, May 29, 1934; *Chem. Abs.*, 1934, 28, 4436.

<sup>4</sup> C. S. Miner and H. J. Brownlee, U. S. P. 1,735,084, Nov. 12, 1929, to Quaker Oats Co.; *Chem. Abs.*, 1930, 24, 630. *British P.* 203,691, 1923; *Chem. Abs.*, 1924, 18, 692. C. S. Miner, J. P. Trickey and H. J. Brownlee, *Chem. Met. Eng.*, 1922, 27, 299, 362. D. H. Killeffer, *Ind. Eng. Chem.*, 1926, 18, 1217. H. J. Brownlee, *ibid.*, 1927, 19, 422.

<sup>5</sup> W. V. Evans and M. B. Aylesworth, *Ind. Eng. Chem.*, 1926, 18, 24. The addition of 10 per cent of sodium chloride increases the extraction of furfural from aqueous solutions 1.5-2 times. Ether, amyl acetate, iso-amyl alcohol and benzene are some of the solvents which can be used as extractants. V. I. Sharkov and I. Belvaevskii, *Lesokhimbicheskaya Prom.*, 1933, 2 (3), 15; *Chem. Abs.*, 1935, 29, 1813. Furfural is itself a solvent. See: J. P. Trickey, *Ind. Eng. Chem.*, 1927, 19, 643. G. Meunier, *French P.* 472,423, 1913; *J.S.C.I.*, 1915, 34, 500. G. Bonnwitt, *British P.* 138,078, 1920; *J.S.C.I.*, 1920, 39, 541A. The analytical reactions of furfural are discussed by: K. Suminokura and Z. Nakahara, *Trans. Tottori Soc. Agr. Sci.*, 1928, 1, 158; *Chem. Abs.*, 1929, 23, 2908. W. J. Powell and H. Whittaker, *J.S.C.I.*, 1924, 43, 35T.

of the simpler aldehydes. In its reactions, according to Miner, Trickey and Brownlee,<sup>6</sup> furfural resembles formaldehyde on the one hand and benzaldehyde on the other. It should be noted that cumarone (see Chapter 5), a substance readily



polymerized to a resin by concentrated sulphuric acid or aluminum chloride, is a furan derivative (benzofuran).

The combination of furan ring and aldehyde group in the structure of furfural permits it to behave chemically as an aldehyde or as an olefin oxide, or to exhibit

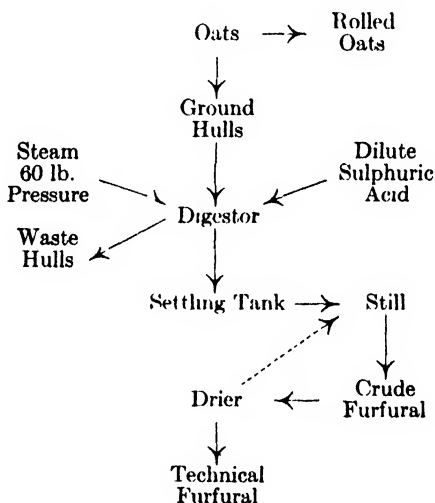


FIG. 85.—Flow Sheet for the Preparation of Furfural from Oat Hulls.

simultaneously the properties of both types of compounds. Like formaldehyde, it reacts with phenols, ketones and amines to give resins; like cumarone, it polymerizes readily. As a consequence, the reactions of furfural are many and diverse.

Furfural is the initial material in the synthesis of a series of compounds containing the furan ring.<sup>7</sup> Thus, furoic acid and furyl alcohol, which have some value as solvents, can be derived from the aldehyde by a Cannizzaro reaction.<sup>8</sup> Kaufmann<sup>9</sup> reduced furfural to furyl alcohol with hydrogen under a pressure of 2

<sup>6</sup> C. S. Miner, J. P. Trickey and H. J. Brownlee, *Chem. Met. Eng.*, 1922, 27, 299.

<sup>7</sup> A discussion of the properties and uses of furfural is given by C. S. Miner, J. P. Trickey and H. Brownlee, *Chem. Met. Eng.*, 1922, 27, 362. For the use of furfural in adhesive compositions, see: H. P. Banks, U. S. P. 1,813,377, July 7, 1931; *Chem. Abs.*, 1931, 25, 5258. F. B. LaForge, *Ind. Eng. Chem.*, 1924, 16, 130. F. B. LaForge, C. W. Tooke, G. H. Mains and W. F. Clarke, *British P.* 207,116, 1923; *Chem. Abs.*, 1924, 18, 1199. B. P. Taylor, U. S. P. 1,566,566, Dec. 22, 1925, to Taylorall, Inc.; *Chem. Abs.*, 1926, 20, 520. Other uses of furfural are given by C. E. Soane, *British P.* 2167, 1915, to Usher-Walker, Ltd.; *Chem. Abs.*, 1916, 10, 2032. *British P.* 169,003, 1920; *J.S.C.I.*, 1921, 40, 780A. German P. 352,521, 1920, to Plausons Forschungsinstitut G.m.b.H.; *J.S.C.I.*, 1922, 41, 720A.

<sup>8</sup> H. Schiff, *Ann.*, 1891, 261, 254. H. Lamprecht, *Ann.*, 1873, 165, 254.

<sup>9</sup> W. E. Kaufmann, *J.A.C.S.*, 1923, 45, 3029.

atmospheres in the presence of a platinum oxide catalyst. Furfural diacetate was isolated by Scheibler, Sotscheck and Friese<sup>10</sup> from a reaction mixture containing furfural, acetic anhydride and glacial acetic acid. Furfural combines with chloral-ammonia.<sup>11</sup> It reacts vigorously with nitrous acid to give resinous products. When the aldehyde is dissolved in ether, however, it is apparently unaffected by this acid.<sup>12</sup>

Mahood and Harris<sup>13</sup> condensed m-tolylene-diamine sulphate with furfural in alcoholic solution and obtained tetra-amino-ditolyl-furyl-methane sulphate which could be hydrolyzed by 6 N hydrochloric acid at 140°C. to diamino-dimethyl-furyl-dihydro-acridine. Acetaldehyde and furfural, in the presence of magnesium methoxide or aluminum ethoxide, give isoamyl pyromucate.<sup>14</sup> Substitution of isobutyraldehyde for acetaldehyde furnishes furyl isobutyrate. Phenol and furfural in boiling dilute acid solutions give a 71 per cent yield of a mixture of o- and p-hydrophenyl-furyl-carbinol.<sup>15</sup> In an alkaline solution of sodium sulphite the yield is cut down to 5 per cent.

The resin-forming properties of furfural were noted by Stenhouse<sup>16</sup> in 1840 and Fownes<sup>17</sup> in 1845. Both these workers called attention to the development of resinous bodies when furfural was boiled with acids or alkalis. Persoz<sup>18</sup> and Stenhouse<sup>19</sup> obtained gummy and tarry substances while investigating the action of furfural on aromatic amines and phenols. Claisen,<sup>20</sup> a few years later, produced a brown resin of indefinite composition by treating furfural with  $\beta$ -naphthol in glacial acetic acid solution, using hydrochloric acid as a condensing agent. In none of these cases was any study reported either of the reaction or of the resinous product aside from a superficial examination of its physical properties.

Resin and tar formation is observed in the preparation and reactions of many derivatives of furfural, and this may be taken as an indication of the ease with which compounds of the class undergo condensation and polymerization. Thus, Beaucourt<sup>21</sup> obtained a dark resin on heating furfural and formamide in a stream of carbon dioxide. Hydrogenating furfural in acetic acid, with a zinc-copper couple, gave a little furyl alcohol and a large proportion of resins.<sup>22</sup> Diphenyl-furylmethane, prepared by Mahood and Aldrich,<sup>23</sup> changed into a gum when kept for a few days. Tetrahydro-furfural, in acetic acid solution, combines with phenylhydrazine to form a hydrazone, the latter being an oily substance which easily resinifies.<sup>24</sup> The reaction of methylmagnesium iodide or phenylmagnesium bromide, as well as analogous organo-metallic compounds, with furylacetone was found to yield resinous substances.<sup>25</sup> Yet another example is the oxidation of furan with 6-10 per cent peracetic acid in acetic acid, which gives a resin of the formula  $(C_4H_5O_2)_n$ .<sup>26</sup>

<sup>10</sup> H. Scheibler, F. Sotscheck and H. Friese, *Ber.*, 1924, 57, 1443; *Chem. Abs.*, 1925, 19, 278. H. Friese, *Ber.*, 1931, 64, 2109; *Brit. Chem. Abs. A.*, 1931, 1289.

<sup>11</sup> R. Schiff and G. Tassiani, *Ber.*, 1877, 10, 1787.

<sup>12</sup> A. Wurtz, "Dict. de Chim. Suppl.," I, 845.

<sup>13</sup> S. A. Mahood and C. R. Harris, *J.A.C.S.*, 1924, 46, 2810.

<sup>14</sup> R. Nakai, *Biochem. Z.*, 1924, 152, 258; *Chem. Abs.*, 1925, 19, 2807.

<sup>15</sup> A. E. Porai-Kochitz, N. A. Kudrjatzev and B. E. Maschkileizon, *J. Appl. Chem. Russ.*, 1933, 6, 685; *Brit. Chem. Abs. A.*, 1933, 1166.

<sup>16</sup> Stenhouse *Ann.*, 1840, 35, 301.

<sup>17</sup> Fownes, *Ann.*, 1845, 54, 52.

<sup>18</sup> Persoz, *Wagner's Jahresberichte*, 1850, 487.

<sup>19</sup> Stenhouse, *Proc. Roy. Soc.*, 1870, 18, 537.

<sup>20</sup> Claisen, *Ann.*, 1887, 237, 272.

<sup>21</sup> K. Beaucourt, *Monatsh.*, 1928, 49, 1; *Chem. Abs.*, 1928, 22, 3409.

<sup>22</sup> J. Wiemann, *Compt. rend.*, 1934, 198, 2263; *Chem. Abs.*, 1934, 28, 6104.

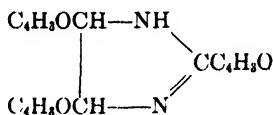
<sup>23</sup> S. A. Mahood and H. Aldrich, *J.A.C.S.*, 1930, 52, 4477.

<sup>24</sup> H. Scheibler, F. Sotscheck and H. Friese, *Ber.*, 1924, 57, 1443; *Chem. Abs.*, 1925, 19, 278.

<sup>25</sup> N. M. Maxim, *Bull. soc. chim.*, 1931, (4) 49, 887; *Chem. Abs.*, 1931, 25, 5424.

<sup>26</sup> J. Böseken, C. Vermij, H. Bunge and C. van Meeuwen, *Rec. trav. chim.*, 1931, 50, 1023; *Brit. Chem. Abs. A.*, 1931, 1422.

The action of potassium amide, in liquid ammonia solution, on furine



results in the formation of tar and hydrogen.<sup>27</sup> Peters and Fischer<sup>28</sup> prepared a series of alkylfurylcarbinols and found that all such compounds resinified on treatment with phosphorus pentachloride, acetyl chloride, benzoyl chloride, concentrated hydrochloric acid or on exposure to light and air. Nitrogen substituted  $\beta$ -furyl-valeramides have been hydrolyzed to the corresponding acids with 20 per cent alcoholic potassium hydroxide. With concentrated hydrochloric acid, on the other hand, hydrolysis was accompanied with resin formation.<sup>29</sup> A sulphur derivative of furan, 2-furylthiol, sealed in a glass tube and kept for a year, changed into a viscous oil and a white solid,  $(\text{C}_5\text{H}_4\text{OS})_n$ . Pure furan compounds appear to be less likely to change on keeping than impure samples.<sup>30</sup> Kirner<sup>31</sup> reported that on adding thionyl chloride to a mixture of furyl alcohol and pyridine, and heating, a black tar was formed.

This reactivity of furan derivatives is also in evidence in the case of halogenated compounds, as, for example, the transformation of 2-bromomethylfuran into a resin in the cold.<sup>32</sup> Furylbromoethylene resinifies in the air, and furylethylene polymerizes rapidly especially in the presence of oxygen and light.<sup>33</sup> The resinous substance obtained from furan by treatment with acid is converted into humic acids by molten caustic potash.<sup>34</sup> Carter<sup>35</sup> recorded the formation of tars during the preparation of furylmalic acid.

#### GENERAL PROPERTIES OF SEVERAL SPECIES OF FURFURAL RESINS

Synthetic resins from furfural possess several properties that limit their use. In general, they are dark in color and do not harden as rapidly with hexamethylene-tetramine as the phenol-formaldehyde type. Preparative details also present problems, since acid catalysts give insoluble, infusible resins as the result of fast, difficultly-controlled reactions.

Mains and Phillips<sup>36</sup> investigated some of the properties of furfural-amine and furfural-ketone resins. They reported that the products did not have sharp fusion points but softened gradually until fluid. The softening points ranged between 25-100°C., but could be raised by increasing the reaction temperatures or heating the reaction mixture for longer periods of time. All of the resins were practically insoluble in water, somewhat soluble in turpentine, quite soluble in benzene, acetone and alcohol, and very soluble in furfural.<sup>37</sup> The acetone, benzene and furfural solutions gave varnish stains which ranged in color from golden brown to black, depending on the resin type, the concentration of the solution and the number of coats applied. The surfaces thus coated have a glossy appearance.

<sup>27</sup> H. H. Strain, *J.A.C.S.*, 1930, 52, 1216.

<sup>28</sup> F. N. Peters and R. Fischer, *J.A.C.S.*, 1930, 52, 2079.

<sup>29</sup> N. Maxim and I. Zugravescu, *Bull. soc. chim.*, 1934, (5) 1, 1087; *Chem. Abs.*, 1935, 29, 1415.

<sup>30</sup> H. Gilman and A. Hewlett, *Iowa State Coll. J. Sci.*, 1930, 5, 19; *Chem. Abs.*, 1931, 25, 4263.

<sup>31</sup> W. R. Kirner, *J.A.C.S.*, 1928, 50, 1955.

<sup>32</sup> H. Gilman and C. Vernon, *J.A.C.S.*, 1924, 46, 2577.

<sup>33</sup> C. Moureu, C. Dufraisse and J. R. Johnson, *Ann. Chim.*, 1927, 7, 14; *Chem. Abs.*, 1927, 21, 2896.

<sup>34</sup> J. Marcusson, *Mitt. Materialprüf.*, 1922, 40, 245; *J.S.C.I.*, 1923, 42, 327A.

<sup>35</sup> A. S. Carter, *J.A.C.S.*, 1923, 50, 2299.

<sup>36</sup> G. H. Mains and M. Phillips, *Chem. Met. Eng.*, 1921, 24, 661.

<sup>37</sup> Tetralin is recommended as a solvent for furfural resins (*J.S.C.I.*, 1922, 41, 568R).



## POLYMERIZATION OF FURFURAL AND REACTIONS WITH OTHER ALDEHYDES

Furfural, like many other aldehydes, undergoes polymerization on standing. Transformation is slow but can be greatly accelerated by heat or the presence of catalysts. Trickey and Miner<sup>38</sup> treated the aldehyde at 100°C. with ferric chloride, aluminum chloride, lead acetate or iron pyromucate (1 per cent of the weight of furfural). As the reaction proceeded, a soft viscous resin formed first and changed into a fusible, semi-solid mass which was soluble in acetone. On further heating, an infusible solid resulted. Reaction was accelerated by heating under pressure and at higher temperatures.

Metallic iron, nickel, lead, magnesium, zinc or tin in the absence<sup>39</sup> or the presence<sup>40</sup> of an acid also catalyzed polymerization. Thus, 100 parts (by weight) of furfural are mixed with 500 parts of 18 per cent hydrochloric acid, 200 parts of water and 250 parts of iron powder. The mixture is allowed to stand until hydrogen is no longer evolved. The resin is obtained by extraction with alcohol.

When furfural is treated with one-fifth of its weight of concentrated sulphuric acid, it is transformed into a gelatinous material which becomes dense and hard and is characterized by a glossy finish and lustrous fracture.<sup>41</sup> Acids in general cause a similar resinification. Porous products, stated to be nonresinous, are obtained according to Snelling<sup>42</sup> by treating 60 parts of furfural with 15 parts of hydrochloric acid and 25 parts of water for a period of 7 days at room temperature. The soluble components are removed by washing with water, and the residue is suggested for use as an absorbent and in the preparation of artists' crayons.

Alkaline catalysts also effect the resinification of furfural. Meunier<sup>43</sup> refluxed 7 parts of a 17 per cent solution of sodium hydroxide and 1 part by weight of furfural. The solution became dark brown. After heating for an hour, it was acidified with hydrochloric acid which precipitated a black, alcohol-soluble resin. Alcoholic solutions of the latter may be employed for coating purposes, giving a firm glossy surface on drying. Better yields of resin are secured by heating the alkali and aldehyde in an autoclave at 140-150°C. A similar procedure was followed by Mains and Phillips<sup>44</sup> employing a 25 per cent solution of sodium hydroxide and concentrated hydrochloric acid (sp. gr. 1.19).

Resins may be prepared by condensing furfural with acetaldehyde,<sup>45</sup> formaldehyde, benzaldehyde or crotonaldehyde in the presence of hydrochloric acid.<sup>46</sup> As an example, 20 parts (by volume) of technical furfural are mixed with 10 parts of acetaldehyde and 5 parts of concentrated hydrochloric acid and poured into a mold maintained at about 20°C. The mixture turns brownish black and solidifies in 2 days giving a homogeneous solid mass. The cast pieces, which resemble ebonite, are washed free of acid and dried gradually. The final material is insoluble in the common solvents and is resistant to the action of acids and alkalis.

<sup>38</sup> J. P. Trickey and C. S. Miner, U. S. P. 1,665,233, Apr. 10, 1928, to Quaker Oats Co.; *Chem. Abs.*, 1928, 22, 1803.

<sup>39</sup> C. S. Miner and J. P. Trickey, U. S. P. 1,665,234, Apr. 10, 1928, to Quaker Oats Co.; *Chem. Abs.*, 1928, 22, 1803.

<sup>40</sup> K. Lüdecke and L. Mamlock, German P. 307,822, 1919, to Vereinigte Chem. Werke A.-G.; *J.S.C.I.*, 1920 39, 273A.

<sup>41</sup> L. T. Richardson, U. S. P. 1,682,934, Sept. 4, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 3999.

<sup>42</sup> W. O. Snelling, U. S. P. 1,716,606, June 11, 1929; *Chem. Abs.*, 1929, 23, 3783.

<sup>43</sup> G. Meunier, *Les matières grasses*, 1916, 9, 4516; *Chem. Abs.*, 1916, 10, 2805.

<sup>44</sup> G. Mains and H. Phillips, *Chem. Met. Eng.*, 1921, 24, 681.

<sup>45</sup> On exposure to light, the reaction products of furfural and acetaldehyde (viz., furalacrolein and its homologues) tend to form resins which are insoluble in alcohol (W. König, *Ber.*, 1925, 58, 2506).

<sup>46</sup> H. Kappeler, U. S. P. 1,373,999, Aug. 23, 1932, to Soc. anon. pour l'ind. chim. & Bâle; *Chem. Abs.*, 1932, 26, 6081. British P. 345,891, 1929; *Chem. Abs.*, 1932, 26, 2073. French P. 697,169, 1930; *Chem. Abs.*, 1931, 25, 2822. Swiss P. 146,561, 1929; *Chem. Abs.*, 1932, 26, 2287. German P. 539,475, 1930; *Chem. Abs.*, 1932, 26, 2073.

## RESINS FROM VARIOUS FURFURAL DERIVATIVES

Like furfural, furyl alcohol resinifies when heated alone or with a catalyst. In the absence of a catalyst, a temperature of 170°C. is necessary; but with 0.1 per cent of hydrochloric acid polymerization takes place at 80°C.<sup>47</sup> Houtz and Adkins<sup>48</sup> reported that a mixture of the ozonides of two octylenes known as "disobutylene" act as catalysts in the polymerization of furyl alcohol. The furyl alcohol resins are stated to be useful for the impregnation of fibrous materials, incorporation in varnishes or as binders for hot and cold molding operations.

By dissolving furyl alcohol in an equal proportion of furfural with 0.1 per cent of hydrochloric acid and heating to 80°C., Miner and Trickey<sup>49</sup> procured a viscous, tacky resin that could be admixed with fillers. The speed of the reaction and the extent to which it proceeds depends on the temperature employed, which should not exceed 110°C. A related composite resin is also prepared by dissolving a furfural resin in an equal amount of furyl alcohol and heating.

A lacquer composition containing a solution of cellulose nitrate in amyl acetate, a plasticizer (castor oil or shellac), sulphuric or hydrochloric acid and furyl alcohol is described by Fawkes.<sup>50</sup> As the lacquer dries, furyl alcohol is converted into a jet-black material with a glossy finish. Trickey<sup>50</sup> obtained a black color on wood or molded articles by treating with furfural and allowing hydrochloric acid to act on the latter.

Furylethylene may be polymerized by heating for 6 hours at 180-190°C. with catalysts such as benzoyl peroxide, potassium chlorate, ozone or linseed oil acids.<sup>51</sup> Dissolved in toluene together with tricresyl phosphate and nitrocellulose, the resin is used as a coating composition.

## FURFURAL AND PHENOLS

The reaction between furfural and phenols in the presence of acid catalysts yields infusible insoluble resins that frequently have a rubbery nature. The materials exhibit elasticity under compression but possess no tensile strength, thus resembling factice (see Chapter 60). The color of the acid-catalyzed reaction products ranges from brown to black. If aqueous hydrochloric acid is added to a mixture of about equal parts of furfural and phenol, a violent reaction ensues, resulting in the formation of an elastic jelly-like substance or a hard, brittle and infusible resin. The nature of the final material depends upon the proportion of hydrochloric acid employed, temperature and other conditions. Phenol-furfural condensation in the presence of acids is complicated by the fact, already noted, that furfural itself readily polymerizes under these reaction conditions. Inasmuch as the utility of a resin, either in varnishes or plastic compositions, depends upon its being soluble or fusible, the products of the phenol-furfural condensation have only a limited use unless the reaction is carefully controlled. Beckmann and Dehn<sup>52</sup> found, however, that rigid, infusible articles could be made by casting the acid-catalyzed

<sup>47</sup> C. S. Miner and J. P. Trickey, U. S. P. 1,665,235, Apr. 10, 1928, to Quaker Oats Co.; *Chem. Abs.*, 1928, 26, 1863.

<sup>48</sup> R. C. Houtz and H. Adkins, *J.A.C.S.*, 1931, 53, 1058.

<sup>49</sup> J. P. Trickey and C. S. Miner, U. S. P. 1,665,237, Apr. 10, 1928, to Quaker Oats Co.; *Brit. Chem. Abs. B*, 1928, 419.

<sup>50</sup> C. E. Fawkes, U. S. P. 1,732,124, Oct. 15, 1929, to Quaker Oats Co.; *Chem. Abs.*, 1930, 24, 252.

<sup>51</sup> J. P. Trickey, U. S. P. 1,627,939, May 10, 1927; *Chem. Abs.*, 1927, 21, 2174. See also British P. 234,862, 1924, to Quaker Oats Co.; *Chem. Abs.*, 1926, 20, 997.

<sup>52</sup> B. E. Sorenson, U. S. P. 1,911,722, May 30, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 3952. British P. 349,442, 1930, to Imp. Chem. Industries, Ltd.; *Brit. Chem. Abs. B*, 1931, 728. See also Chapter 11.

<sup>53</sup> E. Beckmann and E. Dehn, *Sitzber. preuss. Akad. Wiss., Berlin*, 1918, 1201; *Chem. Abs.*, 1920, 14, 642.

products of the phenol-furfural reaction. The procedure is limited in application, as the hydrochloric acid present attacks the moldwalls and causes the casting to stick.

The problem, then, is to make the primary furfural condensate in a fusible, soluble form so that it may find application in solution or in molding compositions with substances that will effect the final curing on subjection to heat and pressure. When an acid catalyst is used, a phenol-furfural resin having these properties is obtainable only if a large excess of phenol is used initially. Thus, if ten times as much phenol as furfural is employed (with a hydrochloric acid catalyst), a liquid is obtained from which the excess phenol may be removed by steam distillation leaving a black, fusible resin. Beckmann and Dehn<sup>55</sup> found that equal parts of furfural and phenol represent the combining proportions for resinification. The addition of strong acid to such a mixture, however, gives an infusible product. Although dilution with phenol results in the formation of soluble, fusible resins, such is not the case with many other organic liquids used as diluents. The action appears to be a specific one for phenol and a few other substances. The large proportion of phenol required materially increases the cost of production.

As furfural may be obtained almost water-free, phenol-furfural resins in contrast to the phenol-formaldehyde types can be prepared in the absence of water, save that formed during condensation. Because of their dark color, the resins can be applied in insulation without the addition of pigments which might tend to impair their electrical properties.

Beckmann and Dehn<sup>56</sup> added concentrated hydrochloric acid to a solution of phenol and furfural and noted that a reddish-violet color changing to dark blue appeared. The mixture becomes hot and finally solidifies to a hard black mass insoluble in acids, alkalies, chloroform, acetone or benzene and unaffected by boiling. The product is scratched slightly by gypsum and strongly by calcite and thus corresponds in hardness to Bakelite C. It possesses some elasticity, breaking with difficulty. The fracture is conchoidal. The resin can be turned on a lathe but attacks metals because of the phenol and acid present. This defect is overcome by heating, which makes the material harder but more brittle.

Beckmann and Dehn studied various mixtures of furfural and phenol to determine the most reactive proportions. The results of these observations are shown in Table 31. It was noticed that after addition of the acid solidification took place first along the walls of the vessel and the surface of the liquid. As a result of a series of experiments it was concluded (as already noted) that the best resin-forming proportions were equal parts of furfural and phenol. A study of a solution of this composition showed that the speed of reaction increased rapidly as the concentration of the acid was raised over a small range. Other reactions of furfural in the presence of hydrochloric acid with hydroxyl-containing aromatic compounds and terpenes were determined by Beckmann and Dehn, and the results were as follows:

1. *o-Cresol*. The solution becomes blue-violet and heats spontaneously, soon solidifying to a black product.

2. *m-Cresol*. This likewise heats but becomes dark blue and condenses to a black solid.

3. *p-Cresol*. The solution becomes green, then blue and finally black. It remains liquid longer than the two other cresols but condenses to a solid substance. It does not heat spontaneously.

4. *Crude Cresol*. (From tar oil.) The solution heats strongly, becoming reddish-violet; and after about an hour becomes hard and black.

<sup>55</sup> E. Beckmann and E. Dehn, *loc. cit.*

<sup>56</sup> E. Beckmann and E. Dehn, *loc. cit.*

TABLE 31.—*Reactions of Phenol and Furfural.*

Duration of Treatment	10% Furfural	20% Furfural	30% Furfural	40% Furfural	50% Furfural	60% Furfural	75% Furfural
10 min.	initial coloration blue changing to dark green						
1 hour	black, liquid, soluble in alcohol with dark green color	black, liquid, almost completely soluble in alcohol with brown color	black, liquid, partly soluble in alcohol with brown color	black, liquid, only partly soluble in alcohol with brown color	black, solid, elastic, almost insoluble in alcohol (dark green color)	black, liquid, partially soluble in alcohol with greenish black color	black, liquid, partially soluble in alcohol with greenish black color
2 hours	liquid	liquid	liquid	solid, elastic	solid, less elastic	solid, elastic like 40% furfural	solid, elastic like 60% furfural
3 hours	liquid soluble in alcohol	liquid	liquid	solid	solid	solid	solid
3.5 hours		liquid	solid, like gelatine	solid	solid	solid	solid
5.5 hours		liquid, almost wholly soluble in alcohol	solid, very elastic	solid	solid	solid	solid
7 hours		liquid	solid	solid	solid	solid	solid
8 hours		liquid	solid	solid	solid	solid	solid
24 hours		solid, like gelatine, almost insoluble in alcohol	solid	solid	solid	solid	solid
30 hours		solid	solid	solid	solid	solid	solid

5. *Thymol*. The solution changes from blue to black and soon thickens to a solid. There is no spontaneous heating.

6. *Pyrocatechol*. The solution turns gradually with spontaneous heating from a reddish-violet to blue and then to black. The separated solid condensation product is lustrous and shows a slight separation of pyrocatechol.

7. *Resorcinol*. The solution reacts immediately and violently with ebullition on the addition of hydrochloric acid. A solid substance, full of bubbles, separates.

8. *Hydroquinone*. One part of hydroquinone dissolves completely in an equal amount of furfural on heating. Hydrochloric acid is added to the warm solution and after cooling, a solid black substance is found, to the surface of which some separated hydroquinone is clinging.

9. *Guaiacol*. At the beginning the solution is brown but becomes black, remaining liquid for a long time and finally solidifying. The solution does not heat spontaneously.

10. *Pyrogallol*. Reaction takes place violently with blackening and the rapid formation of a vesiculated mass.

11. *Phloroglucinol*. It dissolves in furfural only on heating. The addition of hydrochloric acid to the hot solution brings about a violent reaction with ebullition and the separation of a vesiculated brittle substance.

12. *m-Chlorophenol*. The solution becomes dark green and reacts slowly, condensing finally to a hard lustrous solid. There is no heating.

13. *p-Chlorophenol*. The solution becomes dirty gray and eventually black, with the separation of a soft and friable substance.

14. *o-Nitrophenol*. A yellowish-green oil separates, which remains liquid and shows only slight indications of black particles. There is no evolution of heat.

15. *p-Nitrophenol*. The solution becomes brown and then black without the evolution of heat. It remains liquid for a long time but finally solidifies to a product which is not homogeneous. It is admixed with unchanged nitrophenol and is friable.

16. *Picric Acid*. There is no visible reaction even on warming. The dark green mixture remains liquid.

17. *p-Amidophenol*. This dissolves in furfural only on heating and reacts without the addition of acid.

18. *Menthol*. A green solution which becomes darker on warming and then black is produced. Finally a black spongy mass separates which does not become solid.

19. *Terpineol*. The solution becomes brown without spontaneous heating. Later its color turns red and a solid is formed.

20. *Carvacrol*. A reddish-violet solution is yielded which soon heats spontaneously and after 2 hours becomes solid. The product is fairly hard.

21. *Camphor*. The solution reacts very slowly with a reddish-violet coloration, gradually becoming brownish.

22. *Borneol*. Borneol (1 part) dissolves completely in the cold in 2 parts of furfural. The solution is colored violet on the addition of hydrochloric acid, then brownish-black while a solid substance separates. There is no self-heating, and unchanged borneol remains.

23.  *$\alpha$ -Naphthol*. The solution immediately becomes red, turning to violet; and with a violent, almost explosive reaction, changes to a black solid. It is unusually hard but vesiculated.

24.  *$\beta$ -Naphthol*. It reacts immediately with the appearance of a dark blue coloration, but the reaction is less violent than in the case of  $\alpha$ -naphthol. However, there is a strong evolution of heat. The reaction product is hard and lustrous

In certain instances, substitution in the para position with respect to the hydroxyl group appears to be unfavorable for condensation.

Of the foregoing products the most promising ones were from phenol, crude cresol, guaiacol, carvacrol and  $\beta$ -naphthol. All were made in the proportion of 10 parts furfural, 10 parts of the phenolic substance and 1 part of concentrated hydrochloric acid. In manufacturing these resins on a large scale, probably only the products from phenol and crude cresol (or possibly naphthol) can be considered because of the cost.

In place of aqueous acid, alcoholic hydrochloric acid may be used to produce firm black bodies. These have a conchoidal fracture and machine well, but differ from those made in aqueous acid by having a lustrous surface of fracture through-

out the mass instead of in the outer zone only. Other inorganic acids may be employed, but organic acids as acetic, tartaric and benzoic acid (with the possible exception of oxalic acid), exhibit little catalytic action, and the solution of reactants remains liquid even after heating for a long time. Reaction mixtures treated with acetic and benzoic acid did not show a black coloration.

It was noticed in 1872 by Baeyer<sup>54</sup> that an indigo-blue substance, soluble in water, precipitated from mixtures of furfural and phenol, resorcinol and pyrogallol acid on the addition of hydrochloric acid. Steinitzer<sup>55</sup> obtained a hard-rubber substitute by heating 100 g. of furfural, 50-100 g. of phenol and 3 g. of concentrated sulphuric acid in a closed mold at 150°C.

Trickey, Miner and Brownlee<sup>56</sup> found oxalic acid to be less active as a catalyst than sulphuric or hydrochloric acids. External heat was necessary to cause reaction. The results of their observations on hydrochloric acid as a catalyst are summarized as follows:

1. In order to obtain an infusible, insoluble resin the proportions should be preferably slightly in excess of 1 mol furfural to 1 mol phenol.

2. The resin obtained with an excess of phenol was soluble in acetone and alcohol, and remained jelly-like when cooled, even after it had been heated for a number of days.

3. The resins obtained with varying amounts of acid as a condensing agent were similar, but the time necessary to complete the reaction varied from 2 weeks in the case of 0.2 per cent to 10 hours in the case of 0.6 per cent acid, indicating that the acid catalyst is most effective within a very narrow range of concentration.

Tzonev and Yavnel<sup>57</sup> reported that condensation products of better quality were prepared by substituting cresols for phenol. The reaction velocity of furfural with phenols increases in the order: quinol, catechol,  $\beta$ -naphthol, phenol, p-cresol, o-cresol, m-cresol,  $\alpha$ -naphthol, resorcinol. These investigators also stated that the hardest resins were formed from the least symmetrical molecules.

Sweeney<sup>58</sup> produced resins by treating corncobs (ground to pass a quarter-inch mesh) with cresol in the presence of 10 per cent of hydrochloric acid. The weight of cresol was about 60 per cent that of the pentosan-containing corncobs. After heating for 3 hours at 100°C., the mixture yields a black sticky mass which sets to a brittle solid in 48 hours and is then molded. The water-solubility of the resin is decreased by heating at 100°C. for several days.

Jet-black resins, which may be used either alone or with filling materials, are made by developing a small quantity of coloring matter in the phenolic reagent (through condensation with a limited portion of furfural) before formaldehyde treatment.<sup>59</sup> Thus, 1 mol of phenol or cresol is mixed with 0.05 mol of furfural and 1 per cent of hydrochloric, sulphuric or oxalic acid. The mixture is boiled until it blackens, 0.6 mol of formaldehyde is added and the heating is continued to complete the reaction. The black resin is soluble in organic solvents and may be used in varnishes. Hexamethylenetetramine may be substituted for formaldehyde as the hardening agent.

As a means of preparing stable resin solutions that would set at a controllable rate on the addition of an acid catalyst, Knapp<sup>60</sup> suggested the use of a mixture of phenol and phenol-formaldehyde condensates with furfural. A composition of

<sup>54</sup> A. Baeyer, *Ber.*, 1872, 5, 25.

<sup>55</sup> F. Steinitzer, German P. 305,624, 1917; *Chem. Zentr.*, 1920, 2, 495.

<sup>56</sup> J. P. Trickey, C. S. Miner and H. J. Brownlee, *Ind. Eng. Chem.*, 1923, 15, 65.

<sup>57</sup> N. Tzonev and N. Yavnel, *Maslobono Zhirnoye Delo*, 1932 (9), 38; *Chem. Abs.*, 1933, 27, 3471.

<sup>58</sup> O. R. Sweeney, U. S. P. 1,797,551, Mar. 24, 1931, to Iowa State College of Agriculture; *Chem. Abs.*, 1931, 25, 2822. Cf. N. Tzonev and N. Yavnel, *Maslobono Zhirnoye Delo*, 1931 (11), 22; *Chem. Abs.*, 1932, 26, 4493.

<sup>59</sup> C. A. Nash, U. S. P. 1,524,995, Feb. 3, 1925, to Bakelite Corp.; *Chem. Abs.*, 1925, 19, 1061.

<sup>60</sup> P. Knapp, U. S. P. 1,884,747, Oct. 25, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1221.

this sort is made by first refluxing 25-175 parts of formaldehyde and 210 parts of phenol in the presence of hydrochloric acid, cooling, removing water and neutralizing the residue. Then, 140 parts of furfural together with 20-30 per cent of a filler (asbestos) are incorporated giving a stable paste. When the composition is to be used, a small proportion of a catalyst consisting of 70 parts of concentrated sulphuric acid and 30 parts of ethyl alcohol is added; and the mass gradually stiffens, remaining workable for about an hour.

Novotny and Kendall<sup>61</sup> also prepared fusible phenolic condensation products by reacting 100 parts of phenol with 15-40 parts of furfural and 5-10 parts of 39 per cent hydrochloric acid under pressure. Considerable heat is developed and cooling is necessary to maintain a temperature of about 93°C. The mixture is agitated for one hour, and is then heated to 166°C. to remove hydrochloric acid and the water formed by the condensation. Unreacted phenol is eliminated by steam or vacuum distillation. Alkali is added to neutralize any traces of acid remaining. The fusible product is mixed with 8-40 per cent of furfuramide; and, after hardening, the resin may be used in powder form or in alcohol or acetone solution. The dry composition becomes rigid and infusible when subjected to pressure at temperatures of 93-177°C.

Cracked petroleum distillates, having a relatively high content of unsaturated hydrocarbons, may be combined<sup>62</sup> with furfural to give synthetic resins. A cracked gasoline fraction (250 parts by volume) refluxed with 150 parts by volume of technical furfural in the presence of 1 per cent by weight of sulphuric acid furnishes a jet-black jelly-like mass that can be mixed with wood flour and molded. Cracked oils pre-treated with air or other oxidizing gases similarly react with furfural yielding resins, the properties of which depend to some extent on the kind and duration of pre-oxidation. By extracting the cracked distillates with liquid sulphur dioxide the more highly unsaturated portion is isolated and may be freed of solvent by evaporation. After mild oxidation, this extract will form a hard resin with furfural. Catalysts suggested for the resin-forming reaction are sulphuric acid, hydrochloric acid, sodium hydroxide and ammonia.

**Chlorides as Condensing Agents.** In view of the activity of hydrochloric acid as a condensing catalyst for the phenol-furfural reaction, other chlorides were investigated by Beckmann and Dehn.<sup>63</sup> Sodium or potassium chloride had no effect even after prolonged boiling; but ammonium chloride and amine hydrochlorides, on the contrary, catalyzed condensation. A black coloration on heating was noted when 10 per cent of ammonium chloride was added to mixtures of furfural and phenol, crude cresol or  $\alpha$ -naphthol. Compositions containing this type of agent, however, remain liquid in spite of prolonged boiling. A phenol-furfural solution to which 10 per cent of hydroxylamine hydrochloride is added undergoes a violent reaction with the formation of a black solid. Aniline hydrochloride is a less effective catalyst. Metallic chlorides of an acidic nature (zinc, aluminum and cuprous chlorides) behave like the amine hydrochlorides. Epichlorohydrin, acetylene tetrachloride and carbon tetrachloride have been suggested also as condensing agents.<sup>64</sup>

**Basic Condensing Agents.** As noted earlier in the chapter, acid catalysts cause the phenol-furfural reaction to proceed rapidly to the formation of infusible products and thus limit their commercial utilization. Basic catalysts, however,

<sup>61</sup> E. Novotny and D. S. Kendall, U. S. P. 1,398,146, Nov. 22, 1921; *Chem. Abs.*, 1922, 16, 843.

<sup>62</sup> R. B. Day, U. S. P. 1,933,715, Nov. 7, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1934, 28, 664. The use of other aldehydes with petroleum distillates (R. B. Day, U. S. P. 1,933,716, Nov. 7, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1934, 28, 664) is discussed in Chapter 23.

<sup>63</sup> E. Beckmann and E. Dehn, *loc. cit.* See also A. Hutin and P. Dauplin, French P. 491,364, 1919.

<sup>64</sup> Swiss P. 85,076 and 86,308, 1920, to Bakelite G.m.b.H.; *Kunststoffe*, 1921, 11, 62. F. Steinitzer, Austrian P. 86,764, 1921, to Bakelite G.m.b.H.; *Chem. Zentr.*, 1922, 4, 714.

produce a slower, more controllable action by means of which stable intermediate condensates of a fusible and potentially hardenable nature are obtainable. Resins prepared with basic catalysts, therefore, have a greater practical significance.

When equal parts of phenol and furfural are heated with sodium hydroxide, or sodium carbonate solutions, a brown oil forms.<sup>66</sup> The oil thickens on heating for 8 hours at 180°C. in a sealed tube. Under the same conditions a solution of ammonia gives a plastic mass which is soluble in hot alcohol, acetone and chloroform, and is resistant to acids and alkalis. Materials of a similar nature are obtained by heating phenol-furfural mixtures at 100°C. for 3-4 hours with solid alkali hydroxides or carbonates. The brown gummy masses dissolve in organic liquids and, in alcohol and benzene, give clear brown varnishes. They melt easily and at high temperatures become insoluble and infusible, resembling the substances obtained with acids or chlorides.

Trickey, Miner and Brownlee<sup>66</sup> also report fusible furfural resins could be prepared readily by employing alkaline catalysts. Their observations are summarized as follows:

1. In order to obtain an insoluble resin the proportions should be about 1.25 mols of furfural to 1 mol of phenol. With these resins cold-molded products were produced on a commercial scale.

2. The resins formed in an excess of phenol were solid and brittle when hot, melted easily and were readily soluble in acetone, alcohol and furfural.

These investigators stated that sodium hydroxide or the monohydrate of sodium carbonate (1 per cent of the mixture) gave a solution in which the reaction was easily controlled.

Equimolecular proportions of the two reactants in the presence of 4 *N* sodium hydroxide, 3.6 *N* potassium hydroxide or 18 per cent of calcium oxide appeared to give the best yield of a soluble black resin, according to Routala and Kuula.<sup>67</sup> The time required for condensation varied from 2.5 to 4 hours. It was found that furfural resins could be bleached to a considerable degree by halogens.

Nash, Trickey and Miner<sup>68</sup> suggested that a solid catalyst be employed. Thus, a mixture of 94 parts of phenol, 104 parts of furfural and 1 per cent (of the total weight) of sodium carbonate was heated until a stiff plastic mass was formed. When cooled, it could be thinned with additional furfural, admixed with asbestos, molded and finally hardened at 180-230°C.

Two per cent of potassium carbonate (on the basis of the weight of phenol) as a catalyst in the reaction of phenol (100 parts) and furfural (75 parts) were recommended by Novotny and Kendall.<sup>69</sup> The reactants are heated for 2 hours at 130-150°C., water and excess phenol are then removed, and the product is pulverized. The rate of formation of the resin was increased by the addition of about 1 per cent of *p*-phenylenediamine, the solubility of the resin at the same time being decreased. Incorporation of 8 per cent of furfuramide with the powdered resin accelerated its hardening during hot molding.<sup>70</sup> If the reaction mixture is rapidly chilled, condensation is checked and syrupy products are obtained.<sup>71</sup>

<sup>66</sup> E. Beckmann and E. Dehn, *loc. cit.*

<sup>67</sup> J. P. Trickey, C. S. Miner and H. J. Brownlee, *Ind. Eng. Chem.*, 1923, 15, 65. G. Meunier (French P. 23,831, addn. to French P. 472,384; *Kunststoffe*, 1922, 12, 164) also obtained resinous products from the reaction of phenol and furfural in the presence of bases or basic salts. The products could be used in varnishes.

<sup>68</sup> O. Routala and O. Kuula, *Acta Chem. Fennica*, 1931, 4, 50; *Chem. Abs.*, 1931, 25, 5047.  
<sup>69</sup> C. A. Nash, J. P. Trickey and C. S. Miner, U. S. P. 1,736,047, Nov. 19, 1929, to Quaker Oats Co.; *Chem. Abs.*, 1930, 24, 698.

<sup>70</sup> E. E. Novotny and D. S. Kendall, U. S. P. 1,705,495, Mar. 19, 1929, to J. S. Stokes; *Chem. Abs.*, 1929, 23, 2309.

<sup>71</sup> E. E. Novotny and D. S. Kendall, U. S. P. 1,705,496, Mar. 19, 1929, to J. S. Stokes; *Chem. Abs.*, 1929, 23, 2309. See also British P. 243,470, 1924, to J. S. Stokes; *Chem. Abs.*, 1926, 20, 3827.

<sup>72</sup> E. E. Novotny, U. S. P. 1,737,121, Nov. 26, 1929, to J. S. Stokes; *Chem. Abs.*, 1930, 24, 740.



These may be stored and resinified as required with hardening agents and filling materials. A golden-brown, alcohol-soluble resin, designed for use in varnishes, is prepared by refluxing for 1.5-2.5 hours a composition containing (by weight) 2600 parts of commercial cresol, 1300 parts of furfural, 1240 parts of formaldehyde and 13 parts of potassium carbonate.<sup>73</sup>

Ellis<sup>73</sup> prepared fusible, alcohol-soluble resins by condensing furfural and phenol in the presence of carbonates.

As an example, 10 parts (by weight) of phenol, 7.5 parts of furfural and 0.5-1 part of sodium or potassium carbonate are mixed and refluxed for 2-3 hours at 150°C. Residual phenol and furfural are then removed by heating to 160-170°C. and blowing steam through the mixture, which also deodorizes the product. During this treatment the resin becomes more viscous and when cool may be powdered. To prepare a molding composition from the resin, 100 parts by weight are dissolved in alcohol and 3-10 parts of hexamethylenetetramine and 100 parts of wood flour are added. The dry mixture may be molded at 160-180°C. under a pressure of 1000-2000 lb. per square inch. An insoluble and infusible resin can be obtained directly by using a larger proportion of furfural and heating for longer periods.

Kurath<sup>74</sup> made a quick-setting resin by permitting phenol to react with furfural in the presence of sodium hydroxide. The mixture is maintained at such a temperature that the water formed during the reaction is continuously removed. In this manner, lowering of the boiling point due to the accumulation of water is avoided and the reaction is quickened.

Interaction of cresol and furfural may be carried out in two stages.<sup>75</sup> In the first, the aldehyde (100 parts by weight) and cresol (100 parts) are refluxed at 110°C. with calcium hydroxide (12 parts) for an hour. This product does not solidify on cooling. In the second stage the hot resin is mixed with an additional 20 parts of calcium hydroxide and the heating is continued at 150°C. for 15 minutes or until a sample forms a hard brittle mass on cooling. Stearic acid, or a non-hardening resin, may be incorporated in the mixture during the second stage.

A reactive phenol-furfural resin may be added to a mixture of calcium oxide and hexamethylenetetramine to form a mass which is said to cure quickly.<sup>76</sup> For example, 100 parts (by weight) of furfural, 100 parts of phenol and 2 parts of sodium carbonate are heated under reflux for 2 hours and then heated in an open vessel to drive off water. The dehydrated resin is mixed with 8 parts of lime and 1-4 parts of hexamethylenetetramine and heated at 140°C. until a viscous fusible resin is produced.

According to Mains<sup>77</sup> commercial coal-tar acid containing about 75 per cent of m- and p-cresol, 20-25 per cent of xylol and a small proportion of o-cresol is superior to cresylic acid for condensation with furfural in the presence of sodium carbonate. A furfural-formaldehyde mixture can be used in place of furfural.

The plasticity and molding quality of phenol-formaldehyde resins may be improved by the incorporation of furfural.<sup>78</sup> Furfural-phenol resins do not show the same reactivity when incorporated with hexamethylenetetramine as do formal-

<sup>73</sup> E. E. Novotny, U. S. P. 1,771,508, July 29, 1930, to J. S. Stokes; *Chem. Abs.*, 1930, 24, 4648.

<sup>74</sup> Carleton Ellis, U. S. P. 1,771,033, July 22, 1930; *Chem. Abs.*, 1930, 24, 4648.

<sup>75</sup> F. Kurath, U. S. P. 1,969,890, Aug. 14, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1934, 28, 6330.

<sup>76</sup> G. W. Miller, U. S. P. 1,717,614, June 18, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 4090. See also British P. 326,884, 1928, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 4945. German P. 525,092, 1928; *Chem. Abs.*, 1931, 25, 4139. French P. 669,865, 1929; *Chem. Abs.*, 1930, 24, 1997.

<sup>77</sup> British P. 859,047, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1932, 32. French P. 697,753, 1930; *Chem. Abs.*, 1931, 25, 8186.

<sup>78</sup> G. Mains, U. S. P. 1,835,910, Dec. 8, 1931, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1932, 26, 1144.

<sup>79</sup> F. P. Brook, U. S. P. 1,609,506, Dec. 7, 1926, to Bakelite Corp.; *Chem. Abs.*, 1927, 21, 333. Canadian P. 261,953, 1926; *Chem. Abs.*, 1926, 20, 3544.

dehyde-phenol products, hence hardening does not take place rapidly in the mold.<sup>70</sup> Sticking presents another difficulty. Furfural resins have been used in the manufacture of printing plates and matrices, but in these applications it is customary to interpose a thin sheet of tinfoil between the mold and the molded piece to avoid sticking.

The following procedure is suggested by Thompson<sup>70</sup> for securing adhesion between rubber and smooth metal surfaces. A heat-reactive resin (formed by condensing 50 parts by weight of furfural and 50 parts of phenol in the presence of 10 parts of sodium carbonate for 3 hours at 100°C.) is ground and incorporated with powdered rubber. The dry mixture is applied to a metal surface, a layer of vulcanized rubber is added and the whole is vulcanized under pressure.

**Alkaline Salts.** Beckmann and Dehn<sup>71</sup> reported that, in general, alkaline salts did not bring about condensation between phenol and furfural. Numerous tests were made with sodium perchlorate, perborate, thiosulphate and sulphite without obtaining positive results. The solutions of reactants became darker in color on heating but remained liquid. Sodium peroxide ignited the mixture.

**Condensation Without Catalysts.** In the absence of an added catalyst, mixtures of phenol, crude cresol or  $\alpha$ -naphthol and furfural resinify. Beckmann and Dehn<sup>72</sup> heated equal parts of phenol and furfural in a sealed tube for 8 hours at 220°C. The mixture became dark brown, but remained liquid, and was completely soluble in alcohol, acetone and chloroform. A solution composed of equal parts of crude cresol and furfural, heated under the same conditions, gave a thick brownish-black oil containing water globules. The oil was only partly soluble in alcohol but dissolved completely in acetone, chloroform and benzene. When equal parts of  $\alpha$ -naphthol and furfural are heated in a sealed tube for 9 hours at 150°C., a solid product containing bubbles is obtained. This softens without melting and is insoluble in alcohol, acetone, chloroform and benzene.

Novotny<sup>73</sup> also prepared a resin from phenol and furfural without the addition of a catalyst. Equal parts of the reactants give an infusible and insoluble condensation product when heated more than 2 hours at 200-230°C. A fusible material that may be hardened with hexamethylenetetramine is obtained by reducing the heating time to 1 hour and maintaining the same temperature, which is decidedly higher than that (usually not greater than 150°C.) employed with catalysts. Xylenol condenses readily with a mixture of furfural and formaldehyde on refluxing. The temperature in the latter instance is 182-193°C., and water is removed continuously from the condensed vapors by a gravity separator, the reactive ingredients being returned to the digester. The product is admixed with a hardening agent (formaldehyde).<sup>74</sup>

**Modified Furfural Resins. Extending Agents.** A resin designed for use in varnish, molding and insulating compositions is obtained by incorporating phenol-furfural resins with glycerol-phthalic anhydride products.<sup>75</sup> A composition containing a phenol-furfural or aniline-furfural resin, benzene and hydrochloric acid can be used as a protective layer on surfaces coated with cellulose acetate, cellulose nitrate or methyl cellulose.<sup>76</sup> Further condensation of the phenol-furfural resin in sunlight or by baking forms an insoluble, infusible finish that preserves

<sup>70</sup> J. P. Trickey, C. S. Miner and H. J. Brownlee, *Ind. Eng. Chem.*, 1923, 15, 65.

<sup>71</sup> O. A. Thompson, U. S. P. 1,931,309, Oct. 17, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1934, 28, 374. British P. 388,776, 1933; *Chem. Abs.*, 1933, 27, 5900. French P. 723,088, 1931; *Chem. Abs.*, 1932, 26, 4207.

<sup>72</sup> E. Beckmann and E. Dehn, *loc. cit.*

<sup>73</sup> E. Beckmann and E. Dehn, *loc. cit.*

<sup>74</sup> E. E. Novotny, U. S. P. 1,705,493, Mar. 19, 1929, to J. S. Stokes; *Chem. Abs.*, 1929, 23, 2310.

<sup>75</sup> E. E. Novotny, U. S. P. 1,798,715, Feb. 24, 1931, to J. S. Stokes; *Chem. Abs.*, 1931, 25, 2312.

<sup>76</sup> H. Weber, U. S. P. 1,715,688, June 4, 1929, to Westinghouse Elect. & Mfg. Co.; *Chem. Abs.*, 1929, 23, 3822.

<sup>77</sup> C. Dreyfus, U. S. P. 1,904,039, June 26, 1934; *Chem. Abs.*, 1934, 28, 5238.

the cellulose compound from the action of acids, alkalis and heat. A coating composition containing resorcinol dissolved in furfural, tolyl phosphate and cellulose acetate may be resinified on the surface by treatment with hydrogen chloride.<sup>87</sup>

Beckmann and Dehn<sup>88</sup> added 1 part of hydrochloric acid to a cooled solution containing 4 parts of phenol, 4 parts of furfural and 1 part of coal tar. A solid mass similar in properties to the acid-catalyzed resins from phenol and furfural previously described was obtained. A black substance which retained its elasticity up to 100°C. resulted when 5 per cent of lanolin was substituted for the coal-tar. Glycol, glycerol, vaseline, cumarone resin and pyroxylin lacquer could not be used as extending agents because separation occurred during condensation. Sulphur additions gave no beneficial effects.

**Phenol, Furfural and Other Aldehydes.** When equal weights of phenol, formaldehyde and furfural are boiled with 10 per cent of concentrated ammonium hydroxide, a dark liquid separates.<sup>89</sup> Using 10 per cent of aniline hydrochloride, in place of ammonia, somewhat better products are formed. A mixture of phenol, furfural, benzaldehyde and concentrated hydrochloric acid becomes violet and heats spontaneously, gradually becoming black and viscous. The condensate is not solid and yields a soft spongy mass which is partially soluble in organic solvents. A similar but somewhat more solid body is obtained when cresol is substituted for phenol.

Turkington<sup>90</sup> proposed the addition of furfural and a filler to phenol-formaldehyde condensation products in the production of cold-molding compositions. A typical mixture of this sort consists of 40 lb. of finely ground asbestos, 4 lb. of furfural and 8 lb. of phenol-formaldehyde resin. The resin and furfural are first mixed to form a liquid of molasses-like consistency to which the filling material is added.

Incorporation of furfural in phenol-formaldehyde resin varnishes was suggested by Cheetham.<sup>91</sup> As an example, 50 lb. of the resin are dissolved in 100 lb. of alcohol and 20 lb. of furfural. The furfural imparts increased fluidity and penetrating quality to the varnish. The aldehyde also tends to absorb part of the ammonia liberated from hexamethylenetetramine during the setting of the varnish, thus partially preventing the formation of bubbles.

Phenol (50 parts by weight) and formaldehyde (12.5 parts) may be condensed in the presence of hydrochloric acid and treated with furfural (12.5 parts) after removal of water. On heating for 10-12 hours at 80°C., an insoluble resin is obtained.<sup>92</sup> As an alternative, a mixture of phenol, formaldehyde, furfural and catalyst may be stirred together without external heating and allowed to stand. The aqueous layer which settles is separated mechanically, and the mass is heated at 100°C. for a long period. An insoluble resin free from bubble cavities is formed.<sup>93</sup> By allowing a mixture of 50 parts by weight of phenol, 40-60 parts of furfural and 1 part of p-aminophenol to stand and by heating the product (after removing water) for a long period at 70-100°C., an insoluble infusible resin is obtained which may be used in insulation.<sup>94</sup>

<sup>87</sup> A. T. Ward and G. Bray, British P. 320,649, 1928, to Brit Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B, 1929, 1023. Cf. the addition of furfural-phenol resins to cellulose-acetate lacquers, British P. 307,291, 1929, to Brit. Celanese, Ltd.; *Brit. Chem. Abs.* B, 1930, 469.

<sup>88</sup> E. Beckmann and E. Dehn, *loc. cit.*

<sup>89</sup> E. Beckmann and E. Dehn, *loc. cit.*

<sup>90</sup> V. Turkington, U. S. P. 1,508,392, July 29, 1924, to Bakelite Corp.; *Chem. Abs.*, 1924, 18, 2949. Cf. E. Novotny and D. S. Kendall, U. S. P. 1,398,146, Nov. 22, 1921; *Chem. Abs.*, 1922, 16, 843.

<sup>91</sup> H. C. Cheetham, U. S. P. 1,528,006, Mar. 3, 1925, to Bakelite Corp.; *Chem. Abs.*, 1925, 19, 1502. British P. 276,417, 1926; *Chem. Abs.*, 1928, 22, 2476. See also L. V. Redman and H. C. Cheetham, U. S. P. 1,693,939, Dec. 4, 1928, to Bakelite Corp.; *Chem. Abs.*, 1928, 20, 97.

<sup>92</sup> German P. 363,917, 1922, to Felten & Guillaume Carlswerk A.-G.; *J.S.C.I.*, 1923, 42, 275A.

<sup>93</sup> German P. 365,626, 1922, to Felten & Guillaume Carlswerk A.-G.; *J.S.C.I.*, 1923, 42, 615A.

<sup>94</sup> German P. 358,195, 1922, to Felten & Guillaume Carlswerk A.-G.; *J.S.C.I.*, 1922, 41, 948A.

Ellis<sup>96</sup> suggested modifying phenol-butyraldehyde<sup>96</sup> resins by heating them at 150°C. with furfural in the presence of potassium carbonate. He also condensed phenol-acetaldehyde resins (containing excess phenol) with furfural, using alkali carbonates as catalysts.<sup>97</sup> If the condensation of phenol, acetaldehyde and furfural is prolonged until the resinous product when cold can be crushed between the fingers to a non-tacky powder, hexamethylenetetramine may be incorporated and the resultant mixture used for molding.<sup>98</sup> In another process a phenol-formaldehyde resin is heated at 130-150°C. with furfural, calcium oxide, a small amount of hexamethylenetetramine and stearic acid until a brittle, fusible product forms on cooling.<sup>99</sup>

Phenol-furfural resins exhibit a strong tendency to gelatinize before condensation is completed. Hence, the product is likely to be incompletely dehydrated and thus inferior for electrical purposes. To avoid this difficulty, Groff<sup>100</sup> suggested reacting phenol and furfural in the presence of sodium hydroxide at 110-160°C. Then, 30-80 per cent of a phenol-formaldehyde or natural resin is added and heating continued at 150°C. with hexamethylenetetramine as a hardening agent. Varnishes for electrical insulation are prepared from the resulting dehydrated resins by dissolving them in alcohol or butyl acetate. Alternatively, 200 lb. of phenol- or cresol-formaldehyde resin are heated to 140-150°C. and to the fluid resin are added 6 lb. of stearic acid and 16 lb. of calcium hydroxide.<sup>101</sup> The mixture is stirred for 15-30 minutes at 130-150°C. and then 30 lb. of furfural are incorporated. Reaction is continued until a test-sample is brittle when cold. Molding compositions are prepared by mixing the product with hexamethylenetetramine and fillers.

Furfural, even in relatively small proportions, exerts considerable influence on the flowing qualities of the final compositions. By using this aldehyde, it is possible to raise the ratio of filler to resin without affecting the molding properties. Thus, a molding mixture containing 25 per cent of a formaldehyde resin, 20 per cent of furfural and 55 per cent of wood flour exhibits substantially the same flowing qualities as a composition containing equal amounts of resin and filler.<sup>102</sup>

Melhus<sup>103</sup> employed a composition containing a fungicide (e.g., mercuric cyanide), a solution of furfural and a furfural-cresol condensation product for the treatment of plant wounds. Furfural is used in abrasive cements, a typical composition containing 90 parts by weight of sand, 10 parts of phenol-formaldehyde resin, 3.3 parts of furfural and 2.5 parts of alcohol.<sup>104</sup> Phenol-furfural resins, like a number of other types, have been suggested for use in brake linings.<sup>105</sup> Thin sheets of asbestos are treated with graphite or talc and bonded with the resin.

<sup>96</sup> Carleton Ellis, U. S. P. 1,477,870, Dec. 18, 1923; *Chem. Abs.*, 1924, 18, 760.

<sup>97</sup> For the preparation of phenol-aldehyde resins, other than formaldehyde, see Chapter 18.

<sup>98</sup> Carleton Ellis, U. S. P. 1,592,296, July 13, 1926; *Chem. Abs.*, 1926, 20, 3242.

<sup>99</sup> Carleton Ellis, U. S. P. 1,592,773, July 13, 1926; *Chem. Abs.*, 1926, 20, 3242.

<sup>100</sup> British P. 326,545, 1928, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1930, 572. British P. 330,968, 1929; *Brit. Chem. Abs. B*, 1930, 828. G. W. Miller, Canadian P. 298,814, 1930, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 2905. French P. 671,273, 1929; *Chem. Abs.*, 1930, 24, 2317. French P. 670,132, 1929; *Chem. Abs.*, 1930, 24, 1996.

<sup>101</sup> F. Groff, U. S. P. 1,603,112, Nov. 27, 1928, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 722. British P. 323,036, 1928; *Chem. Abs.*, 1930, 24, 2905.

<sup>102</sup> F. Groff and G. W. Miller, U. S. P. 1,720,895, July 16, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 4356. British P. 326,545, 1929; *Brit. Chem. Abs. B*, 1930, 572.

<sup>103</sup> L. V. Redman and V. H. Turkington, U. S. P. 1,716,665, June 11, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 3822.

<sup>104</sup> I. E. Melhus, U. S. P. 1,785,641, Dec. 16, 1930; *Chem. Abs.*, 1931, 25, 5541.

<sup>105</sup> H. O. Keay, U. S. P. 1,650,133, Nov. 22, 1927, to Laurentide Co., Ltd.; *Chem. Abs.*, 1928, 22, 483. Canadian P. 260,334, 1926; *Chem. Abs.*, 1926, 20, 3548. See also British P. 316,189, 1929, to Carborundum Co., Ltd.; *Brit. Chem. Abs. B*, 1931, 65. E. E. Novotny, U. S. P. 1,909,784, May 16, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3795.

<sup>106</sup> R. J. Norton, U. S. P. 1,950,262, Mar. 6, 1934, to Bendix Brake Co.; *Chem. Abs.*, 1934, 28, 3198.

**Impregnation of Paper Moldings.** Beckmann and Dehn<sup>106</sup> obtained a hardened waterproof sheet with good insulating properties by impregnating paper with phenol, furfural and 1-2 per cent of hydrochloric acid. The acid did not cause the paper to become brittle. Solutions of the resin in organic solvents may also be employed.

Furfural resins were used by Novotny in the manufacture of printing plates,<sup>107</sup> phonograph records<sup>108</sup> and in the production of a moldable composite body.<sup>109</sup> In each case, the furfural and phenol condensation products are used to impregnate paper, cloth or other fibrous materials. The resulting material is molded in sheet form. Mains<sup>110</sup> prepared an impregnant by allowing a phenol-furfural resin to react with a solution of furfural in tung oil. Further, phenol-furfural binders may be introduced into paper in the course of manufacture. A proposed application of the resultant sheet is the production of bottle closures. A piece of the material is placed over the bottle, crimped down around the lip and heated to harden the resin, thus making a permanent seal.<sup>111</sup>

Punching and shearing of paper treated with furfural condensates is facilitated by incorporating 0.5-2 per cent of paraffin, beeswax or lanolin in the composition, according to Novotny and Romieux.<sup>112</sup> The impregnation of wood with resins derived from phenolic tars and formaldehyde is assisted by the addition of 2-8 per cent of furfural-chloronaphthalene resins.<sup>113</sup>

#### AMINES AND FURFURAL

Meunier<sup>114</sup> obtained a resin by heating equal parts of aniline and furfural in a closed vessel for 48 hours at 70-80°C. or for 3 hours at 140-150°C. The product was soluble in benzene and alcohol. A 15-20 per cent solution of the resin in benzene, applied as a varnish, gives a brilliant black coating. When spread over a surface and heated at 50-60°C. an insoluble black enamel is formed. Enamel formation can be accelerated by adding zinc chloride as a dehydrating agent.<sup>115</sup>

Mains and Phillips<sup>116</sup> made a more extended examination of the conditions under which the resins described by Meunier are formed, and studied the preparation of soluble resins by the condensation of furfural with a number of amines. The method of attack was to determine first the optimum concentrations of amine and furfural for the formation of a resin at room temperature, i.e., approximately 25°C. When no resins were obtainable at this temperature the optimum concentrations were determined at 100°C. Using the concentrations that gave the best results in the previous experiments, resins were made at 25°C., 100°C. and 150-200°C. Having determined the optimum temperature, the length of time necessary under the given conditions to yield the most satisfactory resin was similarly investigated. The resins of course were not pure compounds, but products of indefinite and varying compositions, and substances exhibiting the same consistency were procured over a rather broad range of temperature by

<sup>106</sup> E. Beckmann and E. Dehn, *loc. cit.*

<sup>107</sup> E. E. Novotny, U. S. P. 1,377,519, May 10, 1921; *Chem. Abs.*, 1921, 15, 3188.

<sup>108</sup> E. E. Novotny, U. S. P. 1,398,148, Nov. 22, 1921; *Chem. Abs.*, 1922, 16, 803.

<sup>109</sup> E. E. Novotny, U. S. P. 1,398,147, Nov. 22, 1921; *Chem. Abs.*, 1922, 16, 802.

<sup>110</sup> G. Mains, U. S. P. 1,841,138, Jan. 12, 1932, to Westinghouse Elect. & Mfg. Co.; *Chem. Abs.*, 1932, 26, 1731.

<sup>111</sup> C. W. Tooke and F. B. La Forge, U. S. P. 1,508,261, Sept. 9, 1924.

<sup>112</sup> E. E. Novotny and C. J. Romieux, U. S. P. 1,557,318, Oct. 13, 1925, to J. S. Stokes; *Chem. Abs.*, 1926, 20, 97.

<sup>113</sup> B. J. Brajnikoff, *Ind. Chimist.*, 1930, 6, 502; 1931, 7, 32, 53, 115, 157; *Chem. Abs.*, 1932, 26, 2842.

<sup>114</sup> G. Meunier, *Les matières grasses*, 1916, 9, 4516; *Chem. Abs.*, 1916, 10, 2803. Amine-furfural resins are also discussed in Chapter 33.

<sup>115</sup> Cf. G. Meunier, French P. 472,384, 1913; *J.S.C.I.*, 1915, 34, 435.

<sup>116</sup> G. Mains and M. Phillips, *Chem. Met. Eng.*, 1921, 24, 661. U. S. P. 1,441,598, Jan. 9, 1923; *Chem. Abs.*, 1923, 17, 1724.

varying the heating period. The criterion of the quality of the resin was simply that it should be hard and fairly brittle when cooled to room temperature, and yet not be noticeably carbonized. Mains and Phillips<sup>117</sup> confirmed the findings of Beckmann and Dehn that hydrochloric acid is an exceedingly effective catalyst in producing resins from furfural and amines or phenols. It not only catalyzes the formation of both fusible and infusible types of resins, but added to furfural alone effects transformation of the aldehyde into an infusible resin.

The results obtained with each compound follow, all proportions being by weight. Unless otherwise stated, reaction is carried on in an open flask, and the product is hard and brittle at 25°C.

*Aniline.* Equal parts of furfural and aniline heated for 1 hour at 200°C. in an open flask or for 3 hours at 170°C. under a reflux give a black resin.

*Aniline hydrochloride.* Equal parts of furfural and aniline hydrochloride heated at 100°C. for 1 hour produce a black resin.

*Aniline and hydrochloric acid.* Five parts each of furfural and aniline and 1 part of concentrated hydrochloric acid (sp.gr. 1.19) give a resin, similar in characteristics to the above, in 10 minutes at 90°C.

*m-Nitraniline.* By heating 1 part of furfural and 2 parts of m-nitraniline at 150°C. for 1.25 hours, a black resin is obtained. If the temperature exceeds 175°C. a violent reaction occurs, voluminous clouds of dense smoke being evolved.

*Cymidine and hydrochloric acid.* Five parts of furfural, 5 parts of cymidine (1-methyl-2-amido-4-isopropylbenzene) and 1 part of hydrochloric acid (sp.gr. 1.19) heated at 150°C. for 10 minutes give a dark reddish-brown resin. In the absence of hydrochloric acid no resin is formed even after heating for 3 hours at 200°C.

*α-Naphthylamine.* When heated for 3 hours at 200°C., 1 part of furfural and 2 parts of α-naphthylamine condense to form a black resin.

*β-Naphthylamine.* One part of furfural and 2 parts of β-naphthylamine mixed at room temperature (25°C.) immediately form a reddish-brown resin.

*o-Toluidine and hydrochloric acid.* By heating 5 parts of furfural, 10 parts of o-toluidine and 1 part of hydrochloric acid (sp.gr. 1.19) for 1 hour at 150°C. a black resin is produced. Without the addition of the hydrochloric acid no appreciable thickening of the liquid is found even after heating for 3 hours at 200°C.

*p-Toluidine.* One part of furfural and 2 parts of p-toluidine heated for 2.5 hours at 150°C. give a black resin.

*m-Toluylenediamine.* Equal parts of furfural and m-toluylenediamine, upon standing overnight at room temperature, 25°C., give a dark brown resin.

*Xylidine and hydrochloric acid.* By heating 5 parts of furfural, 5 parts of xylidine (crude mixed) and 1 part of hydrochloric acid (sp.gr. 1.19) together for 15 minutes at 150°C., a very thick, dark red, almost black, resin is formed.

*Other amines.* No resins were formed by the action of furfural on amylamine, dimethylaniline, diphenylamine and m-phenylenediamine even after heating at 200°C. for three hours. Furfural condensed with the following at room temperature to form crystalline compounds: p-nitraniline, benzidine and toluidine.

Montgomery and Ernst<sup>118</sup> observed that water solutions of furfural as dilute as 2 per cent, mixed with aniline and heated to 125°C. in an autoclave for 15 minutes, yielded resinous bodies similar to the furfural-aniline resins described by Mains and Phillips. The products, however, give a darker coating when applied to wood. When an excess of aniline is used with furfural solution, the residue is

<sup>117</sup> G. Mains and M. Phillips, *loc. cit.*

<sup>118</sup> J. P. Montgomery and E. S. Ernst, *Chem. Met. Eng.*, 1921, 25, 335.

oily and non-brittle at 25°C.; but on steam-distilling the mixture, unreacted aniline is removed and the residue is hard and brittle at 25°C.<sup>119</sup>

The treatment of dilute solutions of furfural with aniline in the presence of a mineral acid or calcium, iron or zinc chloride at 60°C. gives a resin, melting at 150°C., which is further polymerized by heating under pressure at 180-220°C.<sup>120</sup> Huxham<sup>121</sup> found that the furfural-aniline condensate was applicable as a hardening agent for phenol-aldehyde resins. A solution of the latter in benzene or alcohol, to which furfural-aniline resin has been added, may be employed as a binder for cold-molding compositions and as a varnish or enamel. At a temperature of 150°C. this mixture forms a hard, insoluble product. The proportion of furfural-aniline resin may be as high as 90 parts per 100 parts by weight of the fusible phenol resin. A larger ratio renders the resulting material brittle and weak. In making cold-molding compositions naphtha, chloronaphthalenes, oils or waxes together with asbestos or wood flour may be incorporated.

A resin compatible with cellulose nitrate or acetate is prepared by refluxing equimolecular proportions of p-toluenesulphonamide and furfural with 3 per cent of sodium hydroxide for 8 hours at 150°C.<sup>122</sup> The resin which separates is washed and dried. It is soluble in acetone and alcohol, but insoluble in benzene. Incorporation of this resin with lacquers containing cellulose acetate (as the sole constituent) gives films said to be clear, tough and adherent. The cellulose ester-resin mixture may be worked also into blocks or into sheets that can be used in the preparation of laminated glass. Lacquers may also be produced by dissolving a furfural-aniline condensation product in solutions of cellulose acetate.<sup>123</sup> Addition of furfural and aniline to light-sensitive natural or synthetic resins imparts a black color which masks subsequent color changes of the latter.<sup>124</sup>

Interaction of furfural with the reaction product obtained from stearic acid and aniline forms a waxy material which has been suggested as a plasticizer for moldable phenolic condensates.<sup>125</sup> Another resin similarly used as a plasticizer was prepared by Cherry and Kurath.<sup>126</sup> As an example, 30 parts (by weight) of rosin and 10 parts of aniline are heated together for 3 hours, followed by further heating on the addition of 9 parts of furfural. The product is said to be less brittle than rosin. Economies in the use of materials for making furfural-aniline resins have been effected by distilling the reacting mixture *in vacuo* to recover unreacted constituents.<sup>127</sup>

Beaucourt<sup>128</sup> investigated the condensation of furfural (1 mol) with acid amides (2 mols). Crystalline compounds such as furfurylidene-diacetamide were formed in rather low yield, and in the reaction with formamide only resinous products were obtained. The use of hydrochloric acid or pyridine reduced the yield of the crystalline derivative to nearly one-half.

<sup>119</sup> The preparation of water solutions of furfural is very easy, but its fractionation is somewhat difficult (K. P. Monroe, *Ind. Eng. Chem.*, 1921, 13, 133), and there is always a considerable percentage, frequently up to 8 and 10 per cent, of furfural in the rejected water. If its production is being carried on with a view to subsequent condensation with aniline, it would seem useless to prepare anhydrous furfural. If it is being made for other purposes, the rejected water from fractionation may have enough furfural present to make its recovery as furfural-aniline resin profitable.

<sup>120</sup> P. Knapp, U. S. P. 1,696,490, Dec. 25, 1928; *Chem. Abs.*, 1929, 23, 1000.

<sup>121</sup> T. S. Huxham, U. S. P. 1,606,943, Nov. 16, 1926, to American Insulator Corp; *Chem. Abs.*, 1927, 21, 333.

<sup>122</sup> W. H. Moss and B. B. White, U. S. P. 1,840,596, Jan. 12, 1932, to Celanese Corp of America; *Chem. Abs.*, 1932, 26, 1812. For other sulphonamide resins, see Chapter 34.

<sup>123</sup> W. H. Moss and B. B. White, British P. 307,290, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1929, 23, 5338.

<sup>124</sup> W. H. Moss, British P. 303,169, 1927, to British Celanese, Ltd.; *Chem. Abs.*, 1929, 23, 4582.

<sup>125</sup> O. Cherry and F. Kurath, U. S. P. 1,800,815, Apr. 14, 1931, and 1,896,069, Feb. 7, 1933, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1931, 25, 3503; 1933, 27, 3541.

<sup>126</sup> O. Cherry and F. Kurath, U. S. P. 1,894,580, Jan. 17, 1933, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1933, 27, 2592.

<sup>127</sup> French P. 35,202, 1928, to La Fibre Diamond; *Chem. Abs.*, 1930, 24, 2317, addn. to French P. 644,075; *Chem. Abs.*, 1929, 23, 1764.

<sup>128</sup> K. Beaucourt, *Monatsh.*, 1928, 49, 1; *Brit. Chem. Abs. A*, 1928, 766.

## FURFURAMIDE RESINS

Meunier<sup>120</sup> treated furfural with ammonium hydroxide, obtaining furfuramide,  $(C_5H_4O)_nN_3$ ; and then heated the moist product in an autoclave at 120-140°C. for about 3 hours. This procedure gives a brown resin easily soluble in benzene. The benzene solution may be used directly as a varnish, or the resin may be mixed with linseed oil. If ammonium hydrosulphide is substituted for the hydroxide, the resulting substance is a black resin with a disagreeable odor.<sup>130</sup>

Mains and Phillips<sup>131</sup> recommend reacting furfural with ammonium hydroxide and heating the partially dried furfuramide for one hour at 100°C. Trickey, Miner and Brownlee<sup>132</sup> reported that the furfuramide resin of Mains and Phillips was impure furfuralin,  $C_{16}H_{12}O_4N_2$ .<sup>133</sup>

Grinding wheels have been made from a mixture of abrasive grains, gum accroids and a resin derived from furfural and hexamethylenetetramine.<sup>134</sup>

A phenol-formaldehyde-furfuramide condensation product was prepared by Cherry and Kurath<sup>135</sup> by refluxing 200 parts of phenol, 130 parts of formaldehyde and 60 parts of furfuramide until separation into 2 layers had taken place and the odor of formaldehyde was no longer noticeable. The aqueous layer is removed, and the resinous portion is mixed with fillers and molded. Instead of furfuramide, 72 parts of furfural and 30 parts of concentrated aqueous ammonium hydroxide may be used.<sup>136</sup> Hexamethylenetetramine may be substituted for ammonia, in which case the amount of formaldehyde required is reduced. Kurath<sup>137</sup> varied the procedure by first refluxing formaldehyde and phenol with 10 per cent (on the basis of the phenol) of furfuramide. An additional 15-25 per cent of furfuramide is stirred into the mixture and water is removed by decantation. By this method, the possibility of obtaining worthless, rubbery products is reported to be avoided.

As another example of the formation of resins, 200 parts of cresylic acid, 100 parts of furfural and 40 parts of 10 per cent sodium hydroxide solution are refluxed for 4 hours.<sup>138</sup> To the product, 100 parts of formalin are added, and the mixture is boiled for 10 minutes. About 25 parts of furfuramide, sufficient to remove the formaldehyde odor of the composition, are then incorporated. The resulting emulsion may be mixed with fillers, dried and hot-molded. It is essential to keep the proportions of furfural low, if quick-curing products are desired. When relatively larger amounts of furfural are used, however, the reactions may be carried to an advanced stage of condensation, giving materials that still flow well during the molding operation.

<sup>120</sup> G. Meunier, *Les matières grasses*, 1916, 9, 4516; *Chem. Abs.*, 1916, 10, 2805.

<sup>120</sup> A. Cahours (*Ann.*, 1849, 69, 85) obtained thiofurfural by reacting furfural with ammonium sulphide.

<sup>131</sup> G. Mains and H. Phillips, *Chem. Met. Eng.*, 1921, 24, 661.

<sup>132</sup> J. P. Trickey, C. S. Miner and H. J. Brownlee, *Ind. Eng. Chem.*, 1923, 15, 65.

<sup>133</sup> Dubosc (*Le caoutchouc et la gutta-percha*, 1920, 10495; *Kunststoffe*, 1921, 11, 59) found that furfuramide when fused in the absence of air yielded a brown resinous mass consisting for the most part of furfuralin. Bertagnini (*Ann.*, 1853, 88, 128) prepared furfuralin by heating furfuramide at 110-120°C. for one hour, dissolving the resinous mass in alcohol, and precipitating the furfural as the double oxalate. This compound is soluble in boiling water, and is decolorized by treatment with animal charcoal at the boiling temperature, filtered hot, and allowed to crystallize from the filtrate. The furfuralin is liberated by action of potassium hydroxide, and obtained as a white crystalline compound. Furfuralin and formaldehyde give a resin, according to J. Berliner (*Canadian P.* 321,629, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 3392).

<sup>134</sup> E. E. Novotny, U. S. P. 1,909,784, May 16, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3795.

<sup>135</sup> O. A. Cherry and F. Kurath, U. S. P. 1,710,722, Apr. 30, 1929, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1929, 23, 3060. See also *Canadian P.* 280,746, 1928; *Chem. Abs.*, 1928, 22, 3056.

<sup>136</sup> O. A. Cherry and F. Kurath, U. S. P. 1,726,650, Sept. 3, 1929, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1929, 23, 5233.

<sup>137</sup> F. Kurath, U. S. P. 1,726,671, Sept. 3, 1929, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1929, 23, 5233. *Canadian P.* 280,747, 1928; *Chem. Abs.*, 1928, 22, 3056.

<sup>138</sup> O. A. Cherry and F. Kurath, U. S. P. 1,857,357, May 10, 1932, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1932, 26, 2885.



## KETONES AND FURFURAL

**Acetone.** Meunier<sup>139</sup> advocated the acetone-furfural reaction for the production of resins useful for industrial purposes. As an illustration of the preparation of this type of resin, 3.5 parts of an alkali solution containing 1 part by weight of potassium or sodium hydroxide and 2.5 parts of water are refluxed, and during the course of 30 minutes, 1 part of a mixture of equal volumes of furfural and acetone is added. The resin formed is washed while hot with dilute hydrochloric acid and dried. One hundred pounds of furfural yield 140-150 pounds of dry yellow resin. A 20 per cent solution in acetone, benzene or a mixture of 23 parts (by volume) of furfural and 77 parts of alcohol serves as a varnish. The original caustic alkali solution may again be used to resinify additional quantities of furfural and acetone.

A harder and more transparent resin may be obtained by another method. To the caustic alkali solution, which is cooled to prevent overheating and volatilization of the ketone, is slowly added a mixture of acetone and furfural. The reaction mass thickens until a hard paste remains. After removing excess alkali, the resin is heated under pressure for 4 hours in an autoclave. By this procedure, Meunier obtained a light-colored transparent resin. A 20 per cent solution of the product (in benzene, acetone or furfural-alcohol mixtures) gives an almost colorless, brilliant varnish. The resin may be heated also with linseed oil to make an oil varnish.

A somewhat similar process using a stronger solution of alkali was employed by Mains and Phillips.<sup>140</sup> Thus, 1 part of furfural, 1 part of acetone and 2 parts of a 50 per cent sodium hydroxide solution are refluxed for 30 minutes at 100°C., forming a dark-brown solid mass. After washing out excess alkali, drying and cooling, a hard, brittle, brown resin is obtained.

Richardson<sup>141</sup> added 150 parts of furfural and 58 parts of acetone to 40 parts of a 15 per cent sodium hydroxide solution at such a rate that the temperature did not rise above 60°C. The alkaline semi-fluid resin is then washed with dilute phosphoric acid, dried at 100°C. and mixed with naphthalene sulphonic acid and non-alkaline fillers. The final condensation is carried out by heat and pressure in a mold. The quality of white resins from the furfural-acetone condensation is improved, according to Routala and Kuula,<sup>142</sup> by replacing part of the acetone with rosin.

Moss<sup>143</sup> prepared lacquers by using an acetone-furfural resin, cellulose acetate, a volatile solvent, a natural resin (such as manila copal), rosin and diethylphthalate. The lacquers yielded clear, hard and adherent films. Incorporation of furfural-acetone resins with phenol-tung oil-formaldehyde condensate to give a varnish or an impregnating agent has also been described.<sup>144</sup>

**Other Ketones.** A mixture containing 5 parts of furfural, 2 parts of methyl ethyl ketone and 5 parts of 50 per cent sodium hydroxide solution gives a dark-brown gummy mass almost immediately at room temperature (25°C.)<sup>145</sup> By washing with dilute acid, drying at 100°C. and cooling, a hard, brown resin is obtained.

Other ketones which may be condensed with furfural include diethyl ketone,

<sup>139</sup> G. Meunier, *Les matières grasses*, 1916, 9, 4516; *Chem. Abs.*, 1916, 10, 2805.

<sup>140</sup> G. H. Mains and M. Phillips, *Chem. Met. Eng.*, 1921, 24, 661.

<sup>141</sup> L. T. Richardson, U. S. P. 1,584,144, May 11, 1926, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1926, 20, 2082.

<sup>142</sup> O. Routala and O. Kuula, *Suomen Kem.*, 1931, 4, 50; *Brit. Chem. Abs. B*, 1931, 1018.

<sup>143</sup> W. H. Moss, U. S. P. 1,902,256, Mar. 21, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 3350.

<sup>144</sup> British P. 307,289, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1930, 469.

<sup>145</sup> V. Turkington, U. S. P. 1,877,417, July 17, 1928, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 3307.

<sup>146</sup> G. H. Mains and M. Phillips, *Chem. Met. Eng.*, 1921, 24, 661.

vinylethyl ketone, pinacolone, mesityl oxide, phorone, acetophenone, and the ketone mixture present in acetone oil.<sup>146</sup> Solutions of the resins prepared from these compounds may be used as insulating varnishes.

#### MISCELLANEOUS FURFURAL RESINS

**Furfural and Casein.** Substitutes for ivory and horn or materials suggested as insulators are obtained from casein and furfural.<sup>147</sup> A mixture of 50 parts of finely ground casein and 40 parts of wood flour is thoroughly mixed with a solution of 5 parts of tung oil in 5 parts of furfural. The moist plastic mass is then molded at a pressure of 2500 lb. per square inch and temperature of 100°C. for 30 minutes.

Aluminum caseinate may be substituted for casein in condensations with furfural.<sup>148</sup> The caseinate is prepared by dissolving casein in dilute alkali and adding aluminum acetate and a solution of castile soap. Products made with aluminum caseinate are very similar to the casein-furfural resins and it is said can be employed for the same purposes.

**Polymerized Thiofurfural.** Cahours<sup>149</sup> described a compound prepared by the action of hydrogen sulphide on furfuralamide. At low temperatures the reaction yields a white crystalline powder (thiofurfural), but in hot concentrated solutions of furfuralamide, a resinous body forms. Polymerized thiofurfural can be obtained by leading dry hydrogen sulphide into an alcoholic solution of furfural.<sup>150</sup> After several hours a slightly reddish resinous mass, which contains some impurity having a strong odor, separates from the milky liquid. The resin gradually hardens on standing in a desiccator and is soluble in alcohols and benzene. The molecular weight is about 2000, indicating the combination of approximately 20 molecules of the sulphur-containing furfural.<sup>151</sup>

**Furfural Resins Applied in Photography.** Progress in photography has been so linked with the use of silver halide emulsions that it is somewhat surprising to find light-sensitive synthetic resins applied in this field. Beebe, Murray and Herlinger,<sup>152</sup> however, have realized this possibility with furfural-amine resins. By way of illustrating the method, condensation of furfural and concentrated ammonium hydroxide is effected by gentle heating. The resinous product is washed, dried and dissolved in benzene or acetone. This solution is used to apply a thin film of the resin to the surface on which the photographic print is to be made, and printing is done either by optical projection or by contact, exposing for 1-5 minutes. The image is developed in a 25 per cent solution of benzene in turpentine. The sensitivity may be roughly doubled by adding a small percentage of iodoform, methyl iodide, iodine or ammonium bichromate. If a furfural-acetone resin is used, contact prints may be made in 10 seconds under an arc light. A mixture of furfural and aniline, applied as a thin film to a surface, becomes resinous

<sup>146</sup> German P. 386,013, 1920, to Plauson's Forschungsinstitut G.m.b.H.; *J.S.C.I.*, 1924, 43, 434.

<sup>147</sup> S. M. Hull, U. S. P. 1,648,179, Nov. 8, 1927, to Western Elec. Co.; *Chem. Abs.*, 1928, 22, 484.  
<sup>148</sup> U. S. P. 1,711,025, Apr. 30, 1929; *Chem. Abs.*, 1929, 23, 3060. Molding compositions containing glue have been rendered infusible by heating with furfural (produced *in situ* from arabinose). C. E. Soane, U. S. P. 1,468,331, Sept. 18, 1923, to Usher-Walker, Ltd.; *Chem. Abs.*, 1923, 17, 3759. *British P.* 166,003, 1920; *J.S.C.I.*, 1921, 40, 780A.

<sup>149</sup> H. S. Snell, U. S. P. 1,678,713, July 31, 1928, to Western Electric Co.; *Chem. Abs.*, 1928, 22, 3747.

<sup>150</sup> E. Cahours, *Ann.*, 1849, 69, 85.

<sup>151</sup> E. Baumann and E. Fromm, *Ber.*, 1891, 24, 2591.

<sup>152</sup> Furfural in alcoholic solution cooled to -5°C., acidified with hydrochloric acid and submitted to the prolonged action of a current of hydrogen sulphide yields a crystalline precipitate of two species of trithiofurfural. One melts at 229°C. and the other at 128°C. The latter is quite readily transformed into the species of higher melting point. By the action of ammonium sulphide in absolute alcohol on furfural another polymer is obtained melting at 90°C. which is insoluble in alcohol. On heating it is decomposed into products similar to the preceding. (A. Wurtz, "Dict. de chim. 2nd Suppl.," IV, 394. E. Baumann and E. Fromm, *Ber.*, 1891, 24, 3591; *Bull. Soc. Chim.*, 8, 950).

<sup>153</sup> M. C. Beebe, A. Murray and H. V. Herlinger, U. S. P. 1,537,269, June 1, 1926, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1926, 20, 2292.

after a 5 minute exposure to an arc light. The resin formed on distilling pyrrole is also about as light sensitive as the furfural-aniline mixture.

A condensation product of furfural (10 parts) and  $\beta$ -naphthylamine (15 parts), made at room temperature and dissolved in naphtha to make a 23 per cent solution, also gives a light-sensitive coating.<sup>153</sup> Five grams of iodoform and 0.5 cc. of eugenol are added to 50 cc. of the naphtha solution to act as a sensitizer. Less light-sensitive films are obtained from  $\beta$ -naphthylamine and benzaldehyde.  $\beta$ -Naphthylamine and formaldehyde, cyclohexanone-furfural, m- or p-toluenediamine-furfural, benzidine-furfural, m-phenylenediamine-furfural and xylydine-furfural are other examples of condensates giving light-sensitive materials. The exposure time for the different films varies from 5-20 minutes.

Lithographic plates may be protected from the distintegrating action of the ink used by applying a furfural-acetone coating (insoluble in benzene and acetone) and hardening with heat.<sup>154</sup>

<sup>153</sup> M. C. Beebe, A. Murray and H. V. Herlinger, U. S. P. 1,587,273 and 1,587,274, June 1, 1926, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1926, 20, 2292. British P. 265,769, 1926; *Brit. Chem. Abs.* B, 1927, 429.

<sup>154</sup> M. C. Beebe and H. V. Herlinger, U. S. P. 1,820,593, Aug. 25, 1931, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1931, 25, 5741.

## Chapter 25

### Ketone Resins

Condensation of ketones with themselves or with aldehydes results in the formation of low- and high-boiling liquids (which may be employed as solvents), resins, and colored soluble and insoluble amorphous powders. Compatibility with cellulose derivatives is a characteristic of some ketone-aldehyde resins. Of the aldehydes, formaldehyde is the most active agent of its kind in effecting resin-yielding condensations. Owing to their water-resisting qualities, hardness and toughness, the resins obtained from cyclohexanone and related cyclic ketones are of special interest. Resins derived from that class of bodies of extraordinarily reactive properties—the ketenes—are mentioned also in this chapter. Should cheap methods of manufacturing ketones be developed, these substances could scarcely fail of utilization, not only in resin production but in many other ways. Of the resins described in the present chapter, that one most immediately available is yielded by the reaction between acetone and formaldehyde.

#### ACETONE

This ketone is a colorless, mobile liquid, boiling at 56.5°C. Large quantities of it are used as a commercial solvent. Formerly, acetone was made by the destructive distillation of wood, but the greater proportion now available is obtained by the fermentation of carbohydrate material. Other methods of preparation include catalytic dehydration of acetic acid and catalytic dehydrogenation of isopropyl alcohol.<sup>1</sup> Crude acetone, from the dry distillation of calcium acetate, often contains a less volatile fraction (acetone oil) which consists of pentanones, hexanones, and higher ketones.<sup>2</sup> In the purification of this fraction, the colored bodies are precipitated as non-volatile resinous material by metallic chlorides, such as magnesium or ferric chloride.<sup>3</sup> When acetone is treated with barium hydroxide, two molecules unite to form diacetone alcohol, a liquid boiling at 163-164°C.<sup>4</sup> In the absence of solvents, diacetone alcohol may combine with more acetone to yield sym-triacetone-dialcohol.<sup>5</sup> These keto-alcohols can be dehydrated to mesityl oxide<sup>6</sup> and phorone,<sup>7</sup> respectively. Both these unsaturated ketones, together with resinous products, are obtained by treatment of acetone with sulphuric acid or caustic soda.<sup>8</sup> Reaction

<sup>1</sup> A review of the methods for the preparation of acetone is given by Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

<sup>2</sup> H. Suida and H. Poll, *Z. angew. Chem.*, 1927, 40, 505; *Chem. Abs.*, 1927, 21, 2661.

<sup>3</sup> French P. 619,857, 1925, to Établ. Lambiotte Frères; *Brit. Chem. Abs. B*, 1928, 594.

<sup>4</sup> J. B. Conant and N. Tuttle, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1921, 1, 45. Diacetone alcohol was prepared by A. Hoffmann (*J.A.C.S.*, 1909, 31, 722, U. S. P. 1,082,424, Dec. 23, 1913; *Chem. Abs.*, 1914, 8, 788. German P. 229,678, 1909; *Chem. Zentr.*, 1911, 1, 275) by refluxing acetone in the presence of calcium hydroxide. Carleton Ellis (U. S. P. 1,701,473, Feb. 6, 1929, to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 1419) obtained the alcohol by treatment of acetone at 30°C. with 0.01-0.02 per cent of an alkali metal hydroxide. Diacetone alcohol is isolated by fractional distillation of the reaction mixture.

<sup>5</sup> R. Leopold and B. Schacke, German P. 481,290, 1925, to I. G. Farbenind. A.-G.

<sup>6</sup> J. B. Conant and N. Tuttle, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1921, 1, 53.

<sup>7</sup> R. Leopold and B. Schacke, German P. 483,823, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1926, 24, 2146.

<sup>8</sup> L. Gmelin, "Handbook of Chemistry," translated by Watts, *Cavendish Society, London*, 1855,

of acetone with methyl ethyl ketone in the presence of hydrogen chloride yields mainly resinous material.<sup>9</sup> Either ketone when heated with hydrogen chloride gives large amounts of brown resin which, according to Herzog and Kreidl,<sup>10</sup> results from the polymerization of mesityl oxide and phorone formed as intermediate products.<sup>11</sup>

Morgan and Hardy<sup>12</sup> heated acetone with 1 per cent caustic soda solution at 180°C. for 3 hours and obtained high-boiling liquids and non-volatile resins. The volatile fraction contained much phorone. Lougovoy<sup>13</sup> used the condensation product, made in the presence of alkali at 100°C., from acetone as a component of paint and varnish removers.

Reduction of phorone in alcohol with sodium amalgam furnishes a viscous oil.<sup>14</sup> By treatment with zinc amalgam and hydrochloric acid, isophorone is converted largely to a resin non-volatile in steam.<sup>15</sup>

### MISCELLANEOUS REACTIONS OF KETONES

Acetone with sulphur or ammonia yields, among other products, a brown resin.<sup>16</sup> Yellow ammonium sulphide in the cold changes it to bis-dithioacetone ( $C_3H_5S_2$ )<sub>2</sub>. Platinum dichloride transforms the ketone into a crude "platinum resin," a dark brown tarry substance.<sup>17</sup> Acetone condenses with pyrrole in the presence of acids,<sup>18</sup> but not of bases,<sup>19</sup> to give an amorphous substance,  $C_{12}H_{10}N_2O$ , and with chloroform and sodium hydroxide to produce a brown sticky mass called chloroacetylulmic acid,<sup>20</sup>  $C_7H_{11}ClO_2$ .

When acetone is mixed with mercuric chloride and dilute aqueous caustic potash and the filtered solution dialyzed, evaporation of the liquid remaining in the dialyzer yields a resinous material whose constitution corresponds to  $2C_3H_6O \cdot 3HgO$ .<sup>21</sup> The same compound is formed by dissolving mercuric oxide in acetone. Solutions of this substance gelatinize on heating or standing. When obtained as a precipitate the particles are gelatinous, but on drying exhibit a resinous nature.

Condensation of acetone with phenyl- $\beta$ -naphthylamine yields a resinous product which can be used as an antioxidant for rubber,<sup>22</sup> and with sulphonated naphthalenes forms wetting agents.<sup>23</sup> Reaction with rape oil and carnauba wax at 90-100°C., in the presence of iron oxide, gives a thick viscous liquid with a high capacity for absorbing water.<sup>24</sup>

9, 14, 47. V. Dumas, *Ann. chim. phys.*, 1832, (2) 49, 208. L. Claisen, *Ann.*, 1876, 180, 4; *J.C.S.*, 1876, 29, 895. L. Varino, "Handbuch der Preparativen Chemie," Ferdinand Enke, Stuttgart, 1914, 2 (2), 71. For similar reactions with the homologues of acetone, see A. Francke and T. Köhler, *Ann.*, 1923, 433, 314; *Chem. Abs.*, 1924, 18, 58; J. Ekeley and W. Howe, *J.A.C.S.*, 1923, 45, 1917; J. Ekeley and M. S. Carpenter, *J.A.C.S.*, 1924, 46, 446; 1926, 48, 2375.

<sup>10</sup> C. V. Gheorgiu, *Bull. Acad. Sci. Roumaine*, 1923, 8, 68; *J.C.S.*, 1923, 124 (1), 538.

<sup>11</sup> W. Herzog and J. Kreidl, *Z. angew. Chem.*, 1922, 35, 643; *Chem. Abs.*, 1923, 17, 1722.

<sup>12</sup> Mesityl oxide and isophorone are also formed during the production of diisobutylene by heating acetone under pressure with zinc chloride. W. Ipatiev, A. Petrov and I. Ivanov, *Ber.*, 1930, 63, 2806.

<sup>13</sup> G. T. Morgan and D. V. N. Hardy, *J.S.C.I.*, 1933, 52, 518.

<sup>14</sup> B. M. Lougovoy, U. S. P. 1,884,765, Oct. 25, 1932, to Chadeloid Chem. Co.; *Brit. Chem. Abs. B.*, 1933, 837.

<sup>16</sup> L. Claisen, *Ann.*, 1876, 180, 9; *J.C.S.*, 1876, 29, 895.

<sup>17</sup> J. W. Baker, *J.C.S.*, 1926, 669.

<sup>18</sup> W. C. Zeise, *Ann.*, 1843, 47, 24.

<sup>19</sup> W. C. Zeise, *Ann.*, 1840, 33, 34, 66.

<sup>20</sup> A. Baeyer, *Ber.*, 1886, 19, 2184.

<sup>21</sup> V. V. Chelintzev and B. V. Tronov, *J. Russ. Phys.-Chem. Soc.*, 1916, 48, 105, 749; *Chem. Abs.*, 1917, 11, 452. H. Fischer, A. Schormüller and R. W. Windecker, *Ann.*, 1932, 498, 284.

<sup>22</sup> W. Hardy, *Jahresberichte*, 1863, 330.

<sup>23</sup> J. E. Reynolds, *Proc. Roy. Soc.*, 1871, 19, 431; *J.C.S.*, 1871, 24, 561.

<sup>24</sup> W. P. ter Horst, U. S. P. 1,870,880, Aug. 9, 1932, to Naugatuck Chemical Co.; *Chem. Abs.*, 1932, 26, 5787.

<sup>25</sup> French P. 630,615, 1927, to Etablissement Kuhlmann; *Chem. Zentr.*, 1928, 1, -1097.

<sup>26</sup> A. Chwala, German P. 456,351, 1923; *Brit. Chem. Abs. B.*, 1930, 430.

Chloroacetone, when treated with potassium hydroxide, is changed to a brown resin.<sup>25</sup> Even on exposure to diffused light it slowly polymerizes to a black rubber-like mass.<sup>26</sup>

### HYDROXY KETONES

Dihydroxyacetone,  $\text{CH}_2\text{OHCOCH}_2\text{OH}$ , is a white material melting at  $82^\circ\text{C}$ . Molecular weight determinations, however, indicate it possesses a bimolecular structure. According to Strain and Dore,<sup>27</sup> x-ray diffraction measurements demonstrate the polymerization of the crystalline monomeric ketone to the dimeric form. Transformation of dihydroxyacetone begins soon after it is prepared and is complete in 25-30 days. From a sample of this ketone which has been stored at ordinary temperatures, Levene and Walti<sup>28</sup> isolated the compounds  $\text{C}_6\text{H}_{10}\text{O}_8$  (m. p.  $164^\circ\text{C}$ .) and  $\text{C}_6\text{H}_8\text{O}_7$  (m. p.  $258^\circ\text{C}$ .) thus indicating that autocondensation (with elimination of water) had occurred. Similar observations were made by Dirschel and Braun<sup>29</sup> with acetoin,  $\text{CH}_3\text{COCHOHCH}_3$ . Monohydroxyacetone (acetol) is reported to polymerize readily but is rendered stable when dissolved in an equal volume of methyl alcohol.<sup>30</sup>

1,2-Dihydroxy-5-hexanone slowly changes to a dimeric form on long standing and when methylated it yields a viscous condensation product.<sup>31</sup> When heated at  $125^\circ\text{C}$ ., in the presence of a small proportion of sulphuric acid, it is converted into a brown resin.<sup>32</sup> Methyl-dihydroxyamyl ketone exhibits similar properties.<sup>33</sup> On boiling diacetone alcohol with solid potash a reddish-brown, easily fusible resin is obtained.

### KETO ACIDS

Pyruvic acid,  $\text{CH}_3\text{COCOOH}$ , is a colorless compound boiling at  $65^\circ\text{C}$ . under 10 mm. pressure. It readily assumes a trimeric form melting at  $92^\circ\text{C}$ .<sup>34</sup> In aqueous solution, the sodium salt of this acid (and also that of laevulinic acid) reacts under pressure at  $230^\circ\text{C}$ . or higher with hydrogen (using an aluminum oxide-nickel catalyst) to give products which, after acidification, resinify quickly in the air.<sup>35</sup> Pyruvic acid and formaldehyde, in alkaline media, furnish trimethylol lactic acid,  $(\text{HOCH}_2)_3\text{CCHOHCOOH}$ .<sup>36</sup> In acid media, a dibasic acid ( $\text{C}_6\text{H}_8\text{O}_8$ ), the alkali and silver salts of which are resinous, and a lactone are obtained.<sup>37</sup> Dehydration of the latter results in the formation of a viscous syrup which changes to a clear hard resin. According to Sen,<sup>38</sup> a saturated solution of potassium hydroxide in ethyl alcohol is the best condensing agent for pyruvic acid and benzaldehyde.

Musajo<sup>39</sup> obtained a vitreous mass when attempting the preparation of a benzilidene derivative of pyruvic acid.

<sup>25</sup> A. Riche, *Compt. rend.*, 1859, 49, 176.

<sup>26</sup> C. F. Allen and W. A. L. Trigg, *Ind. Eng. Chem., News Ed.*, 1931, 9, 184.

<sup>27</sup> H. H. Strain and W. H. Dore, *J.A.C.S.*, 1934, 56, 2649.

<sup>28</sup> P. A. Levene and A. Walti, *J. Biol. Chem.*, 1928, 78, 23; *Brit. Chem. Abs. A*, 1928, 870.

<sup>29</sup> W. Dirschel and E. Braun, *Ber.*, 1930, 63, 416.

<sup>30</sup> P. A. Levene and A. Walti, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1930, 10, 2.

<sup>31</sup> P. A. Levene and A. Walti, *J. Biol. Chem.*, 1930, 88, 771; *Brit. Chem. Abs. A*, 1931, 68.

<sup>32</sup> See also H. Hibbert and J. Timm, *J.A.C.S.*, 1923, 45, 2433.

<sup>33</sup> H. Hibbert and C. P. Burt, *J.A.C.S.*, 1928, 50, 1411.

<sup>34</sup> G. Massol, *Bull. soc. chim.*, 1905, 33, 336; *J.C.S.*, 1905 88 (2), 302.

<sup>35</sup> V. Ipatiev and G. Razuvaev, *Ber.*, 1927, 60, 1973; 1928, 61, 634; *Chem. Abs.*, 1928, 22, 386, 2141.

<sup>36</sup> H. Hosseus, *Ann.*, 1893, 276, 79.

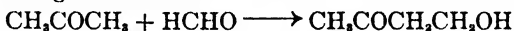
<sup>37</sup> V. Feofilaktov, *J. Russ. Phys.-Chem. Soc.*, 1926, 58, 759; 1929, 61, 1145; *Chem. Abs.*, 1928, 22, 3393; 1930, 24, 832; *Ber.*, 1926, 59, 2765; *Chem. Abs.*, 1927, 21, 896.

<sup>38</sup> R. N. Sen and B. K. Sen, *J. Indian Chem. Soc.*, 1934, 11, 411; *Chem. Abs.*, 1935, 29, 120.

<sup>39</sup> L. Musajo, *Gazz. chim. ital.*, 1932, 62, 901; *Chem. Abs.*, 1933, 27, 1337.

## ALIPHATIC KETONE-ALDEHYDE CONDENSATIONS

**Intermediate Compounds.** The preparation of 3-ketobutanol, or monomethylolacetone, the simplest condensation product from acetone and formaldehyde, is described by Merling and Köhler.<sup>40</sup>

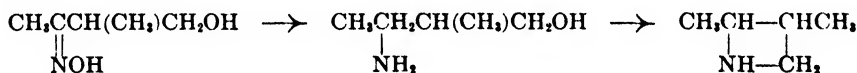


Three kilograms of acetone and 1 kg. of 35 per cent aqueous formaldehyde are condensed in the presence of 20-60 g. of potassium carbonate. When a test portion gives no precipitate after the addition of aniline acetate, the carbonate solution is separated, the mixture is neutralized with acid and filtered to remove the potassium salt. The filtrate is evaporated *in vacuo* at 100°C. and the residue distilled under 30 mm. pressure. 3-Ketobutanol (boiling point 110°C. at 30 mm.) is isolated from the fraction of the distillate which is collected between 95° and 120°C. The residue from the distillation is a very viscous, dark brown liquid. Ketobutanol is a limpid oil, colorless and odorless, miscible with water, alcohol and the usual organic solvents. It polymerizes on long standing to an insoluble viscous syrup, but in the form of its acetate (boiling point 96°C. at 15 mm.) it is quite stable. Methyleneketobutanol is a by-product in the preparation of ketobutanol.<sup>41</sup>

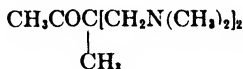
Another procedure is the catalytic dehydrogenation of 1,3-butylene glycol under reduced pressure at 200°C., punice impregnated with a copper compound serving as the catalyst.<sup>42</sup>

Heating ketobutanol with 1 per cent of alkali results in the formation of an infusible resin.<sup>43</sup> This keto-alcohol also reacts with phthalic anhydride at temperatures between 140° and 230°C. to give an orange-colored resin soluble in butyl acetate and compatible with nitrocellulose.

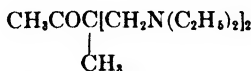
2-Methyl-3-ketobutanol was obtained by Merling and Köhler<sup>44</sup> from methyl ethyl ketone and formaldehyde, following the same procedure as for ketobutanol. Methylketobutanol boils at 90°C. under 18 mm. pressure. This compound does not polymerize as readily as its lower homologue. Reduction of its oxime, followed by heating with a halogen acid, gives 3,4-dimethylcyclobutanimine (3,4-dimethylazetidine).<sup>45</sup>



In the presence of formaldehyde, reaction of 2-methyl-3-ketobutanol with dimethylamine or diethylamine is complicated by further condensation with the aldehyde to yield



and



respectively,<sup>46</sup> two derivatives of therapeutic value.

<sup>40</sup> G. Merling and H. Köhler, U. S. P. 989,993, Apr. 18, 1911, to Farbenfabr. vorm. F. Bayer & Co.; *Chem. Abs.*, 1911, 5, 2305. British P. 19,037, 1909; *J.S.C.I.*, 1910, 29, 1037. French P. 409,403, 1909; *J.S.C.I.*, 1910, 29, 719.

<sup>41</sup> H. Gault and L. A. Germann, *Compt. rend.*, 1933, 197, 620; *Chem. Abs.*, 1934, 28, 106.

<sup>42</sup> British P. 386,897, 1932; *Brit. Chem. Abs. B*, 1933, 260; German P. 568,546, 1931; *Chem. Abs.*, 1933, 27, 2696; French P. 740,647, 1932; *Chem. Abs.*, 1933, 27, 2697, all patents to I. G. Farbenind. A.-G.

<sup>43</sup> Carleton Ellis, U. S. P. 1,557,571, Oct. 20, 1925; *Chem. Abs.*, 1926, 20, 301.

<sup>44</sup> G. Merling and H. Köhler, U. S. P. 981,668, Jan. 17, 1911, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1911, 30, 240. German P. 223,207, 1909; *Chem. Abs.*, 1910, 4, 2980.

<sup>45</sup> German P. 247,144, 1910, to Farbenfabr. vorm. F. Bayer; *Chem. Zentr.*, 1912, 2, 159.

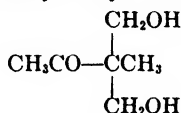
<sup>46</sup> G. Merling and H. Köhler, German P. 254,714, 1911; *J.S.C.I.*, 1913, 32, 380; German P. 266,656, 1911; U. S. P. 1,070,623, 1,071,007, 1,071,008, Aug. 19, 1918; *J.S.C.I.*, 1913, 32, 925; all patents to Farbenfabr. vorm. F. Bayer & Co.

Claisen<sup>47</sup> observed that alkaline agents, such as potassium carbonate or cyanide, caused acetone and acetaldehyde to combine readily even at room temperature. To the product,  $\text{CH}_3\text{CHOHCH}_2\text{COCH}_3$ , he gave the name hydracetylacetone. This compound (also called methyl acetonyl carbinol) has a ketonic odor and the consistency of glycol. It mixes with water in all proportions and boils at  $77-78^\circ\text{C}$ . under a pressure of 19 mm. To prevent resinification, the alkali should be neutralized before removal of unreacted materials by distillation.<sup>48</sup>

Condensation of aldehydes with ketones may take place in the absence of water.<sup>49</sup> To the alkaline mixture prepared by adding 20 parts of powdered potassium hydroxide to 1000 parts of acetone, and maintained at a temperature of  $5^\circ\text{C}$ ., are added 300 parts of acetaldehyde over a period of 6 hours. After 30 minutes longer, carbon dioxide is passed into the solution to precipitate potassium carbonate, which is then removed. Unreacted acetone is separated from the mixture by distillation. The residue contains hydracetylacetone and only a very small proportion of resin.

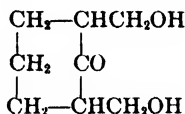
Dimethylol-acetone,  $\text{CH}_3\text{COCH}(\text{CH}_2\text{OH})_2$ , is obtained from 1 mol of formaldehyde and 2 mols of acetone in the presence of aqueous alkali sufficient to yield a pH of not less than 10.<sup>50</sup> Reaction may be carried out in the absence of a condensing agent.<sup>51</sup> A mixture of 8 parts of acetone and 4.2 parts of 30 per cent aqueous formaldehyde are heated at  $100^\circ\text{C}$ . under pressure for 48 hours. Dimethylolacetone is obtained in 76 per cent yield. This compound is not volatile at the above temperature but decomposes at  $180^\circ\text{C}$ . under 16 mm. pressure.

Similar condensations with methyl ethyl ketone also yield a dimethylol com-

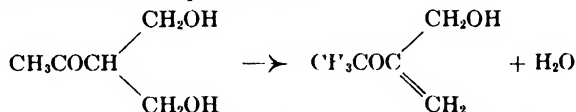


pound, which melts at  $62^\circ\text{C}$ . and boils at  $140^\circ\text{C}$ . under 16 mm. pressure.

The above-mentioned dimethylol derivatives, as well as one from cyclohexanone



can be prepared in absence of catalysts by heating the reactants in an autoclave to  $130^\circ\text{C}$ .<sup>52</sup> If dehydrating agents (e.g., phosphoric acid) are present, one molecule of water is removed yielding a volatile unsaturated keto-alcohol.<sup>53</sup> For dimethylol acetone the reaction can be represented as



Dimethylol-acetone has been used for the impregnation of fabrics and is rendered insoluble by passage of the treated fabric over hot rolls.<sup>54</sup>

<sup>47</sup> L. Claisen, *Ber.*, 1892, 25, 3165. See also, British P. 264,830, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1927, 860.

<sup>48</sup> H. Langwell and J. E. Youell, British P. 390,905, 1932, to British Industrial Solvents, Ltd.; *Brit. Chem. Abs.*, B, 1933, 661. Instances are also recorded of the replacement of acetone by more complex ketones. (J. Salkind, *J. Russ. Phys.-Chem.*, 1905, 37, 486; *Chem. Zentr.*, 1905, 2, 752. J. Colonge, *Bull. soc. chim.*, 1927, 41, 325; *Brit. Chem. Abs.* A, 1927, 449).

<sup>49</sup> A. Knorr and A. Weissenborn, U. S. P. 1,714,378, May 21, 1929, to Winthrop Chem. Co.; *Chem. Abs.*, 1929, 23, 3477; German P. 495,878, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 3516.

<sup>50</sup> W. Flemming and H. D. v. d. Horst, U. S. P. 1,955,060, April 17, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3741. German P. 544,887, 1930; *Chem. Abs.*, 1932, 26, 3521. British P. 361,597, 1930; *Brit. Chem. Abs.* B, 1932, 301.

<sup>51</sup> W. Flemming and H. D. v. d. Horst, German P. 575,949, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4314.

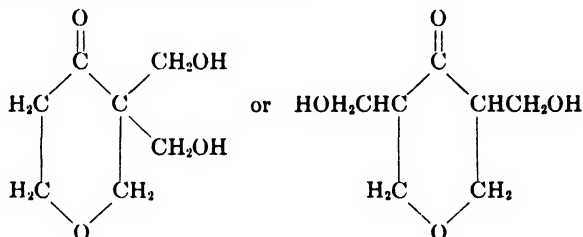
<sup>52</sup> British P. 381,686, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1933, 101.

<sup>53</sup> W. Flemming and H. D. v. d. Horst, German P. 577,256, 1933; *Chem. Abs.*, 1933, 27, 3944. British P. 389,884, 1931; *Brit. Chem. Abs.* B, 1933, 552.

<sup>54</sup> A. Schneevoght and H. D. v. d. Horst, German P. 568,425, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2045. British P. 385,378, 1931; *Brit. Chem. Abs.* B, 1933, 265.

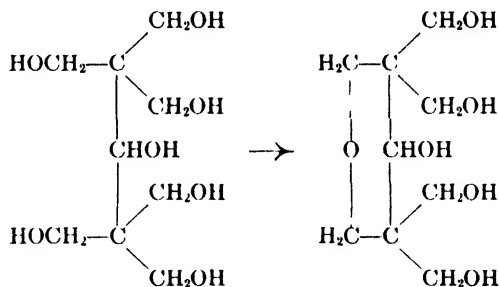


Morgan and Holmes<sup>55</sup> have described the condensation product of 1 mol of acetone and 4 mols of formaldehyde. It was isolated from the reaction mixture of one mol of acetone and two of formaldehyde, after heating with sodium hydroxide. The resulting solution was evaporated on a water bath and the viscous syrupy residue subjected to vacuum distillation. Only 10 per cent was volatile. The non-volatile portion was a brown resin. On further heating, frothing occurred, and the final product consisted of a voluminous, insoluble, friable mass. The distillate contained 3-ketobutanol and a liquid boiling at 164-165° C. (under 20 mm. pressure) which was postulated as 3,3- (or 3,5-) dimethylol-tetrahydro-4-pyrone,



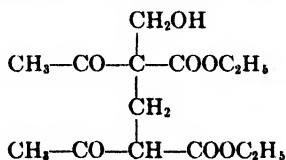
In marked contrast to acetone, methyl ethyl ketone yielded under the same conditions of condensation mostly volatile products consisting of 2-methyl-3-ketobutyl alcohol, the dimethylol compound (2-aceto-2-methyl-trimethylene glycol) melting at 60°C., and higher-boiling viscous liquids. The latter yielded resins when heated with alcoholic alkali. The mono-, di- and trimethylol compounds obtained from diethyl ketone were accompanied by little or no resinous material.

Anhydro-enneaheptitol is the anhydride (m.p. 156°C.) of the heptahydric alcohol resulting from the reaction of 1 mol of acetone with 6 mols of formaldehyde.<sup>56</sup> It is interesting to note that in the presence of a large proportion of formaldehyde, in addition to the six hydrogen atoms in acetone being substituted by (CH<sub>2</sub>OH) groups, the carbonyl group is reduced. The relation of the alcohol to its anhydride can be represented by



Heating acetone and formaldehyde *in vacuo* below the resinifying temperature gives rise to the formation of colorless, viscous products. They may be used as substitutes for glycerol and as dyeing or printing assistants.<sup>57</sup>

Gault and Burkhard<sup>58</sup> reported the production of a viscous substance



<sup>55</sup> G. T. Morgan and E. L. Holmes, *J.C.S.*, 1932, 2667.

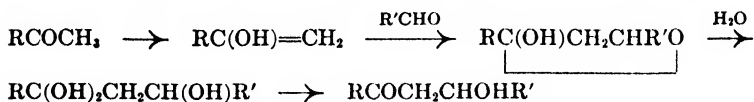
<sup>56</sup> M. Apel and B. Tollens, *Ber.*, 1894, 27, 1087; *Ann.*, 1896, 289, 46. C. Mannich and W. Brose, *Ber.*, 1922, 55, 3185.

<sup>57</sup> British P. 349,856, 1930, to I. G. Farbenind.; *Brit. Chem. Abs. B.*, 1931, 917.

<sup>58</sup> H. Gault and J. Burkhard, *Compt. rend.*, 1924, 199, 795; *Brit. Chem. Abs. A.*, 1924, 1332.

(3-methylol-3,5-dicarbethoxy-2,6-heptandione) on condensing ethyl acetoacetate with formaldehyde. Acetaldehyde yields ethyl  $\alpha$ -ethylolacetoacetate (2-hydroxy-3-carbethoxy-4-pentanone) from which a non-crystalline compound, 4-methyl-3,5-dicarbethoxy-3(1-ethylol)-2,6-heptandione, is obtained by the action of diethylamine at  $-10^{\circ}\text{C}.$ <sup>60</sup>

As a mechanism for the reaction between ketones and aldehydes, Bodendorf and Koralewski<sup>60</sup> suggest that the ketone assumes an enol form which unites with the aldehyde, hydration and dehydration of the latter product yielding the keto-alcohol. These steps can be represented by the following scheme:



**Water-Soluble Products.** Condensation of ketones and aldehydes (chiefly acetone and formaldehyde) yields water-soluble syrups. Stockert and Traxl<sup>61</sup> effected the reaction by using 1 per cent of caustic soda (or more if a diluent was present) at  $15^{\circ}\text{C}.$  To avoid the formation of by-products, smaller amounts of alkali (0.3 per cent initially) were added at 24-hour intervals since it is known that an alkaline catalyst is partly or entirely neutralized in the course of the reaction.

By using disodium phosphate as a condensing agent, Ellis<sup>62</sup> obtained viscous water-soluble syrups which on warming with a small proportion of potassium hydroxide become ivory-colored, rubber-like masses. These can be dried and powdered to yield a whitish substance which chars without melting at  $250\text{--}300^{\circ}\text{C}.$  and is insoluble in the usual organic solvents.<sup>63</sup> When sodium carbonate is the catalyst, a reddish oil separates from the reaction mixture. After it is freed of water, the oil can be dissolved in methyl alcohol and mixed with wood flour and alkaline hardening agents to give a molding composition.<sup>64</sup> In the presence of trisodium phosphate, acetone and formaldehyde give a water-white syrup<sup>65</sup> which may be used in lacquers and varnishes. With 1 mol of acetone to 6 of formaldehyde in alkaline media, a fusible, alcohol-soluble resin is formed.<sup>66</sup>

From acetone, or methyl ethyl ketone, and formaldehyde in alcoholic solution, catalyzed by caustic alkali, Huxham<sup>67</sup> obtained a resin which after heating at  $105^{\circ}\text{C}.$  becomes insoluble in organic solvents and alkali. It may be employed as a protective coating for alkali-storage tanks.

By modifying the conditions of condensation, water-soluble viscous liquids are produced which serve as substitutes for glycerol, for the preparation of "anti-freeze" solutions, for the finishing of textiles, or for the impregnation of paper.<sup>68</sup> For example, Voss<sup>69</sup> prepared a thick, viscous, syrupy, water-soluble liquid (which gave no indication of resinification after being kept for a year) in the following manner: 400 parts of formaldehyde (30 per cent) were mixed with 50 parts of acetaldehyde and 15 parts of acetone and to the mixture were added 12 parts of calcium hydroxide. The temperature was maintained at  $30\text{--}35^{\circ}\text{C}.$  After 12 hours, the alkali was precipitated as the oxalate (with oxalic acid) and water and unchanged aldehyde removed by distillation at  $60\text{--}65^{\circ}\text{C}.$  under reduced pressure.

<sup>60</sup> H. Gault and T. Wendling, *Compt. rend.*, 1924, 199, 1082; *Brit. Chem. Abs. A*, 1925, 65.

<sup>61</sup> K. Bodendorf and G. Koralewski, *Arch. Pharm.*, 1933, 271, 101; *Chem. Abs.*, 1933, 27, 2672.

<sup>62</sup> K. Stockert and W. Traxl, *Austrian P.* 96,433, 1919 and 98,669, 1920; *Chem. Zentr.*, 1925, 1, 2472.

<sup>63</sup> Carleton Ellis, U. S. P. 1,502,945, July 29, 1924; *Chem. Abs.*, 1925, 19, 186.

<sup>64</sup> See also Carleton Ellis, U. S. P. 1,514,509, Nov. 4, 1924; *Chem. Abs.*, 1925, 19, 710.

<sup>65</sup> Carleton Ellis, U. S. P. 1,514,508, Nov. 4, 1924; *Chem. Abs.*, 1925, 19, 710.

<sup>66</sup> Carleton Ellis, U. S. P. 1,716,542, June 11, 1929; *Chem. Abs.*, 1929, 25, 3822.

<sup>67</sup> Carleton Ellis, U. S. P. 1,683,535, Sept. 4, 1928; *Chem. Abs.*, 1928, 22, 3999.

<sup>68</sup> T. S. Huxham, U. S. P. 1,482,929, Feb. 5, 1924, to Carleton Ellis; *Chem. Abs.*, 1924, 18, 1058.

<sup>69</sup> British P. 249,556, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 917.

<sup>60</sup> A. Voss, German P. 875,766, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4890.

Morgan and Holmes<sup>70</sup> obtained a colorless water-soluble syrup from equimolecular proportions of acetone and formaldehyde at 25°C. in the presence of barium hydroxide. After all formaldehyde had reacted, any remaining alkali was neutralized with carbon dioxide and acetone and water were removed *in vacuo*. Distillation of the colorless, extremely viscous residue under high vacuum yielded a considerable amount of distillate and a residual yellowish-brown, friable resin. On fractionation, the distillate gave a colorless oil (boiling at 90-110°C. under 16 mm. pressure) which spontaneously polymerized to a hard, clear resin. This solid possessed machinable properties, and was insoluble in organic solvents. Irradiation by a mercury vapor lamp accelerated polymerization. Prior to the fractionation step, halogens or halogen compounds (e.g., iodine or iodine monochloride) may be added to the distillate.<sup>71</sup>

Mannich<sup>72</sup> condensed acetone and diethyl ketone with formaldehyde in the presence of ammonium chloride to obtain resinous material.

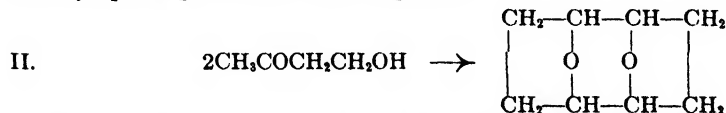
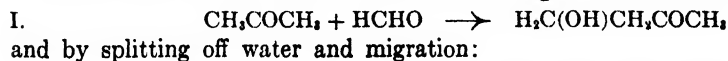
**Werner's Resin.** Werner<sup>73</sup> first called attention to acetone resin. He mixed 40 per cent formaldehyde solution with acetone and found that reaction did not occur until alkali was added. The addition of a small amount of caustic potash to the undiluted reactants caused an immediate and violent action with the separation of an orange-red product. When the substances are mixed in 10 per cent aqueous solution, combination proceeds much more slowly, the alkalinity of the liquid diminishing considerably as the reaction progresses. After an hour the condensation product begins to separate, and after 24 hours the reaction is complete. The resulting orange-colored, amorphous powder is freely soluble in alcohol, acetone and glacial acetic acid, from which solutions it is precipitated unchanged by water. It dissolves sparingly in benzene, chloroform or ether. Werner stated that the same compound is produced whether an excess of acetone or of formaldehyde is used.

A yellow precipitate is obtained by adding hydrochloric acid to the alkaline filtrate. The resin and the yellow precipitate from the filtrate had the empirical formula  $C_6H_8O$ . Werner proved, however, that it is not a polymer of methylene acetone.

Müller<sup>74</sup> also noted that the condensation of acetone with formaldehyde did not give the expected methylene-acetone. With a small proportion of alkali as a condensing agent, ketobutanol was formed. Larger amounts of alkali gave an amorphous compound ( $C_8H_{12}O_2$ ).

Seventy-five grams of 40 per cent formaldehyde solution and 60 g. of acetone are poured into a solution of 50 cc. of 30 per cent aqueous caustic soda and 200 cc. of 96 per cent alcohol, and the reaction mixture cooled. After standing for 36 hours, the reddish-brown solution is poured into 2 l. of water. A yield of 50-55 g. of a brown, non-crystallizable mass having an odor like that of hexanone is obtained. It has no sharp melting point and chars above 300°C. The resin is soluble in ethyl and methyl alcohol (to give neutral solutions), in acetone, glacial acetic acid and benzol. It is less soluble in ether and almost insoluble in ligroin, water and dilute caustic alkali solutions.

Müller stated that there are two distinct stages in the formation of this resin:



<sup>70</sup> G. T. Morgan and E. L. Holmes, British P. 404,317, 1932; *Brit. Chem. Abs.* B, 1934, 244.

<sup>71</sup> G. T. Morgan and E. L. Holmes, British P. 408,063, 1934; *Chem. Abs.*, 1934, 27, 5692. See also *British Plastics*, 1933, 4, 431. G. T. Morgan, A State Exp. in Chem. Res.; *Rep. Brit. Ass. Advancement Sci.*, 1933.

<sup>72</sup> C. Mannich, *Arch. Pharm.*, 1917, 255, 261; *Chem. Abs.*, 1918, 12, 684.

<sup>73</sup> E. Werner, *Proc. Chem. Soc.*, 1904, 20, 196; *Chem. Zentr.*, 1905, 1, 221.

<sup>74</sup> A. Müller, *Ber.*, 1921, 54, 1142; *Chem. Abs.*, 1922, 16, 3449.

This, however, assumes that all the acetone takes part in the reaction. Under similar conditions, experience has shown that much acetone still remains after all the formaldehyde has disappeared.

Iodine-containing condensation products of acetone and other ketones with aldehydes have been suggested by Hertkorn<sup>76</sup> to replace iodoform as a disinfecting powder. One procedure for preparing such compounds is as follows: One hundred grams of acetone and 250 g. of formaldehyde are mixed in 2 l. of water. To this, 30-60 g. of alcoholic soda are added; and the mixture is gently heated until spontaneous reaction sets in and the liquid assumes a yellow color. It is cooled and allowed to stand for 2 days with frequent agitation. An orange-yellow flocculent precipitate is formed. Heating to 50°C. at this stage favors the deposition of the orange powder. The horny mass obtained by treating the orange powder with iodine is insoluble in water, fairly soluble in alcohol, ether and amyl acetate, and very soluble in acetone and other ketones. The product is almost insoluble in cold benzene or turpentine, but is partially soluble in hot benzene.

Ketone resins may be used as modifying agents to decrease the luster of rayon.<sup>76</sup> For example, a finely divided insoluble product, from the condensation of 1 mol of acetone and 6 mols of formaldehyde in the presence of aqueous sodium hydroxide, is incorporated with the cellulose solution before extrusion. The polymer obtained from the reaction of benzaldehyde and acetone may be employed similarly.<sup>76a</sup>

**Molding Compositions.** Plauson<sup>77</sup> proposed the following molding composition: One hundred parts of wood flour or mineral powder are mixed with 58 parts of acetone and 100 parts of 30 per cent formaldehyde. Ammonia gas is then introduced with continual agitation under a pressure of 1-3 atmospheres. Reaction is complete in 10-15 minutes. Excess ammonia is removed and water evaporated *in vacuo*. Another composition is made from 30 parts of acetone-soluble rubber resin dissolved in 60 parts of acetone and 100 parts of 40 per cent formaldehyde. This mixture is incorporated in a mixing-drum with 150-250 parts of wood flour and a 10 per cent alcoholic or aqueous solution of caustic soda is added. Reaction is complete in half an hour without resorting to pressure. Alkali and excess acetone are removed by washing followed by evaporation. The dry powder molded at 150 atmospheres and 200°C. gives articles which are inert to alkalis, acids and almost all organic solvents. At a pressure of 200-250 atmospheres, the molded article more nearly resembles natural wood. Methyl ethyl ketone may be used instead of acetone; but although it forms a resin, it is partially converted into a volatile compound immiscible with water. An aromatic ketone such as benzophenone does not resinify readily with formaldehyde and an alkaline condensing agent.

It is suggested also that the condensation product from 6 mols of formaldehyde and 1 mol of acetone, made in the following manner, be employed in molding operations.<sup>78</sup> One hundred parts of 30 per cent formaldehyde solution are mixed with 9-10 parts of acetone, and 15 parts of 33 per cent sodium hydroxide solution are gradually added with vigorous stirring. The mixture must be cooled after addition of the base. Twenty-nine parts of a light yellow, granular solid ( $C_6H_8O_4$ ) separate. After washing it is almost white. It possesses high insulating powers, is burned with difficulty and is insoluble. The product from 3 mols of formaldehyde and 1 mol of acetone (at 30-60°C.) was an oily resin which could be coupled with diazotized p-nitraniline to form a dark yellow oil-soluble dyestuff.<sup>79</sup>

**Condensation Products in Varnishes.** Plauson<sup>80</sup> attempted to obtain oil-soluble compounds (to be used in varnish) by reacting formaldehyde and acetone (or other aldehydes and ketones) with turpentine or terpene hydrocarbons at

<sup>76</sup> J. Hertkorn, U. S. P. 901,709, Oct. 20, 1908; *Chem. Abs.*, 1909, 3, 530. British P. 17,220, 1908; *J.S.C.I.*, 1909, 28, 1006.

<sup>76a</sup> H. Dreyfus, R. H. J. Riley and J. Bower, British P. 392,621, 1931; *Brit. Chem. Abs.* B, 1933, 621. French P. 42,662, 1933, addition to French P. 702,174; *Chem. Abs.*, 1934, 28, 896.

<sup>76a</sup> British P. 407,545, 1933, to Brit. Celanese, Ltd.; *Brit. Chem. Abs.* B, 1934, 464.

<sup>77</sup> H. Plauson, U. S. P. 1,397,144, Nov. 15, 1921; *Chem. Abs.*, 1922, 16, 629. German P. 337,960, 1922; *Chem. Zentr.*, 1922, 2, 539. British P. 156,137, 1920; *Chem. Abs.*, 1921, 15, 1789. Canadian P. 233,180, 1923; *Chem. Abs.*, 1923, 17, 3237.

<sup>78</sup> H. Plauson, German P. 351,849, 1922; *J.S.C.I.*, 1922, 41, 720A.

<sup>79</sup> H. Plauson, U. S. P. 1,500,844, July 8, 1924; *Chem. Abs.*, 1925, 19, 186. British P. 182,497, 1921; *J.S.C.I.*, 1922, 41, 676A.

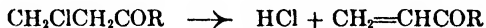
<sup>80</sup> H. Plauson, German P. 389,241, 1920; *J.S.C.I.*, 1924, 43, 434B.

200°C. Alkali sulphides, carbonates or perborates were employed as condensing agents. The products were soluble in the various solvents for natural resins. More soluble resins were obtained by adding a small proportion of phenols or of linseed oil to the reactants.

The initial condensation products of formaldehyde and acetone, after polymerization by treatment with urea, aniline, or other organic bases, can be incorporated with pyroxylin to give a coating composition.<sup>81</sup> Refluxing equimolecular mixtures of acetone and aldol, in the presence of alkali, yields a resin which may be fused with rosin to form a coating material.<sup>82</sup> A modification of the latter procedure consists in adding rosin and hydrochloric acid to the ketone-aldol mixture before refluxing. Diacetone alcohol and formaldehyde also react, in alkaline media, to furnish resins which may be employed as components of varnish and lacquers.<sup>83</sup>

### UNSATURATED KETONES

Compounds possessing a double bond in close proximity to a carbonyl group exhibit enhanced reactivity. Those of the type  $\text{RCOCH}=\text{CH}_2$  polymerize spontaneously in the presence of catalysts. Blaise and Maire<sup>84</sup> prepared a series of unsaturated ketones by boiling the corresponding chloroketones with diethylaniline.



Such ketones are mobile, lachrymatory liquids which polymerize, on standing, to elastic odorless substances and react quickly with alkali to form brown resins. They may be prepared also by the reaction of olefins with acetyl chloride, in the presence of aluminum chloride,<sup>85</sup>



and by dehydration of keto-alcohols with zinc chloride.<sup>86</sup> Methyl vinyl ketone is obtained by the hydration of vinyl acetylene with dilute sulphuric acid, using



mercuric sulphate as a catalyst and an oxidizing agent (e.g., ferric sulphate) as a promoter.<sup>87</sup> Ketones in which the ethylenic linkage is farther from the carbonyl group have been produced by passing mixed vapors of unsaturated acids and saturated acid anhydrides over manganese oxide at 300-500°C., oleic acid and acetic anhydride furnishing heptadecenyl methyl ketone.<sup>88</sup>

Transformation of unsaturated ketones to yellow resins, which may be used in varnishes, is effected by agitation with 1 per cent aqueous sodium oleate at

<sup>81</sup> C. E. Burke, U. S. P. 1,755,099, Apr. 15, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1920, 24, 2905. See also C. E. Burke, Canadian P. 327,820, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 1222.

<sup>82</sup> H. A. Gardner and C. A. Knauss, *Ind. Eng. Chem.*, 1928, 20, 599.

<sup>83</sup> A. E. Maze, U. S. P. 1,683,835, Sept. 11, 1928; *Chem. Abs.*, 1928, 22, 4262.

<sup>84</sup> E. E. Blaise and M. Maire, *Bull. soc. chim.*, 1908, 3 (4), 165; *Chem. Abs.*, 1908, 2, 1824.

<sup>85</sup> S. Krapivin, *Bull. Soc. Imp. Moscow*, 1908, 1; *Chem. Abs.*, 1911, 5, 1281.

<sup>86</sup> G. Merling and H. Köhler, U. S. P. 981,668 and 981,669, Jan. 17, 1911, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1911, 30, 240. See also German P. 222,551, 1908; *Chem. Zentr.*, 1910, 2, 120. British P. 19,088, 1909; *J.S.C.I.*, 1910, 29, 1134. French P. 409,403, 1909; *J.S.C.I.*, 1910, 29, 719, all patents to Farbenfabr. vorm. F. Bayer & Co.

<sup>87</sup> R. F. Conaway, U. S. P. 1,967,225, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5834. British P. 388,402, 1933; *Chem. Abs.*, 1933, 27, 4547; German P. 594,083, 1934; *Chem. Abs.*, 1934, 28, 4436. French P. 719,309, 1931; *Chem. Abs.*, 1931, 25, 3265, all patents to E. I. du Pont de Nemours & Co. See also A. S. Carter, U. S. P. 1,890,161, Feb. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 2453.

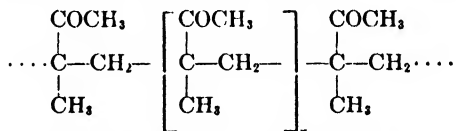
<sup>88</sup> O. Schmidt and K. Huttner, U. S. P. 1,988,021, Jan. 15, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1431.

60°C.,<sup>99a</sup> or by heating in the presence of oxygen or oxidizing agents.<sup>99</sup> For example, Bradley<sup>99</sup> resinified methyl-methylene-acetone by bubbling air through it at 80-100°C. On evaporation of solutions of this resin in benzene, or ketones, very tough films were obtained.<sup>99</sup> At its boiling point, 2 molecules of this ketone combine to give 1-octene-3,7-dione,<sup>99</sup> and on heating with dilute acid or alkaline solutions 1-hydroxy-octane-3,7-dione is formed.<sup>99</sup> When kept for several days at 60°C., mixtures of methyl-methylene ketone and diolefins (in the presence of diethyl-aminoethoxy-oleylanilide) yield rubber-like products.<sup>99</sup> Condensations of methylene ketone with styrene,<sup>99</sup> maleic anhydride<sup>99</sup> and stand oil<sup>99</sup> have been reported.

Either methyleneacetone or methyl isopropenyl ketone is used as a low-boiling solvent with cellulose acetate and a compatible synthetic resin (e.g., a sulphonamide resin)<sup>99</sup> to make a lacquer.<sup>99</sup>

By treating polymerized methylene acetone, dissolved in acetone, with formaldehyde (and hydrogen chloride) a resin is obtained which may be employed as the intermediate layer in safety glass.<sup>100</sup> Also, the secondary polymeric alcohol (made by reduction of the polymerized ketone) may be condensed with formaldehyde.<sup>101</sup> n-Butylene acetone, prepared from n-butyraldehyde and acetone in alkaline media, resinifies when heated with alkali but is relatively stable in the presence of 20 per cent sulphuric acid.<sup>102</sup> The isomeric isobutylene-acetones are, however, unstable under the same conditions and when treated with sodium hypobromite they yield tars.<sup>103</sup>

Isopropenyl methyl ketone, prepared by dehydration of  $\beta$ -methylketobutanol ( $\text{CH}_3\text{COCH}(\text{CH}_3)\text{CH}_2\text{OH}$ ) with potassium pyrosulphate or anhydrous oxalic acid and zinc chloride, slowly polymerizes (in an atmosphere of nitrogen) at room temperature.<sup>104</sup> The polyketone is a hard, tough, glass-like mass similar in properties to eu-polystyrene, and is soluble in organic solvents with extreme swelling. It appears to contain 1400 units and its structure is believed to be:



<sup>99a</sup> K. Meisenburg, German P. 568,907, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2831. British P. 335,185, 1929; *Chem. Abs.*, 1931, 25, 1401.

<sup>99</sup> E. Tschunkur and W. Bock, German P. 555,859, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 6165.

<sup>99</sup> T. F. Bradley, private communication.

<sup>99</sup> The use of resins from methyl-methylene ketone in the manufacture of billiard balls or artificial glass is described in German P. 309,224, 1917, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1920, 39, 624A.

<sup>99</sup> G. Merling and H. Kohler, U. S. P. 991,735, May 9, 1911, to Farbenfabr. vorm. F. Bayer & Co.; *Chem. Abs.*, 1911, 5, 2560. Also German P. 227,176, 1909; *Chem. Zentr.*, 1910, 2, 1421.

<sup>99</sup> G. Merling and H. Kohler, U. S. P. 991,734, May 9, 1911, to Farbenfabr. vorm. F. Bayer & Co.; *Chem. Abs.*, 1911, 5, 2560. German P. 227,177, 1909; *Chem. Zentr.*, 1910, 2, 1421. See also L. Claisen, *Ber.*, 1892, 25, 3164.

<sup>99</sup> British P. 349,976, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 937. French P. 734,985, 1932; *Chem. Abs.*, 1933, 27, 1221.

<sup>99</sup> K. Meisenburg, W. Bock and O. Buchle, U. S. P. 1,937,063, Nov. 28, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1207. German P. 599,058, 1934; *Chem. Abs.*, 1934, 28, 8004. British P. 399,232, 1:33; *Chem. Abs.*, 1934, 28, 1881.

<sup>99</sup> British P. 376,479, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 948.

<sup>99</sup> L. Kolleck and H. Ufer, German P. 538,307, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1558; addn. to German P. 580,234, 1933; *Chem. Abs.*, 1933, 27, 4943. See also Chapter 51.

<sup>99</sup> See Chapter 34.

<sup>99</sup> British P. 359,387, 1930, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B*, 1932, 31.

<sup>100</sup> H. Hopff, German P. 554,668, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 6165.

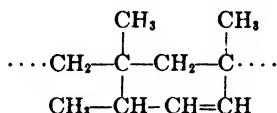
<sup>100</sup> French P. 721,827, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4142. British P. 367,313, 1931; *Brit. Chem. Abs. B*, 1932, 475.

<sup>100</sup> E. N. Eccott and R. P. Linstead, *J.C.S.*, 1930, 905.

<sup>100</sup> R. Locquin and R. Heilmann, *Bull. soc. chim.*, 1929, 45 (4), 1126; *Brit. Chem. Abs. A*, 1930, 325. See also S. G. Powell, *J.A.C.S.*, 1924, 46, 2514. J. Pastureau and Zamenhof, *Compt. rend.*, 1926, 182, 323; *Chem. Abs.*, 1926, 20, 1593.

<sup>100</sup> H. Staudinger and B. Ritzenthaler, *Ber.*, 1934, 67, 1773.

On reduction with hydrogen iodide and phosphorus, the polymer yields the hydrocarbon  $(C_8H_8)_n$  instead of  $(C_8H_{10})_n$ . Apparently cyclization occurs during the latter operation giving



Treatment of the ketone with stannic chloride gives black tarry masses, whereas Florida earth is inactive.

Irradiation of isopropenyl methyl ketone with a mercury-vapor lamp effects transformation to a polymer of 480 units. This substance is much softer than the one containing 1400 units, less swollen by solvents, and can be precipitated as a powder by addition of methyl alcohol to its solution in acetone. At  $100^\circ\text{C}$  isopropenyl methyl ketone isomerizes to the dimeric diketone,



An amorphous glassy mass was obtained by Cox and McElvain<sup>106</sup> on heating 87 g. of benzalmethyl isopropyl ketone,  $(\text{CH}_3)_2\text{CHCOCH}=\text{CHC}_6\text{H}_5$ , with 12 g. of sodium ethoxide.

Furylideneacetone with magnesium methyl iodide or phenyl magnesium bromide yields almost exclusively resinous bodies<sup>106</sup>. Mesityl oxide condenses with acetaldehyde in the presence of aqueous caustic soda,<sup>107</sup> and the product (after removal of the alkali) may be converted into a light-colored, elastic, spirit-soluble resin by heating to  $200^\circ\text{C}$ .

Oleone and hypochlorous acid (in the cold) yield the corresponding chlorohydrin, which reacts with soap to give wax-like products.<sup>108</sup>

Benary, Meyer and Charisius<sup>109</sup> state that although hydroxymethylene ketones (resulting from the condensation of ketones with ethyl formate in the presence of sodium ethoxide) are usually stable, hydroxymethylene-methyl-n-propyl ketone,  $\text{C}_6\text{H}_5\text{COCH}=\text{CHOH}$ , quickly thickens and acquires a red color.

### KETENES

Many attempts have been made to improve the yield of ketene from the pyrolysis of acetone. A variety of catalysts have been employed and yields up to 90 per cent have been reported.<sup>110</sup> Hurd<sup>111</sup> obtained evidence of the formation of methylketene by pyrolysis of both methyl ethyl and diethyl ketones. Other

<sup>106</sup> R. F. B. Cox and S. M. McElvain, *J.A.C.S.*, 1934, 56, 2459.

<sup>107</sup> N. Maxim, *Rull soc. chim.*, 1931, 49, 887; *Brit. Chem. Abs.*, A, 1931, 1069.

<sup>108</sup> H. Deutsch, W. Haehnel and W. O. Herrmann, German P. 433,853, 1922, to Consort. f. Elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs.*, B, 1927, 228.

<sup>109</sup> D. K. Tressler, U. S. P. 1,873,072, Aug. 23, 1932, to Mathieson Alkali Co.; *Chem. Abs.*, 1932, 26, 5965. U. S. P. 1,925,033, Aug. 29, 1933; *Chem. Abs.*, 1933, 27, 5564.

<sup>110</sup> E. Benary, H. Meyer and K. Charisius, *Ber.*, 1926, 59, 110; *Chem. Abs.*, 1926, 20, 1590.

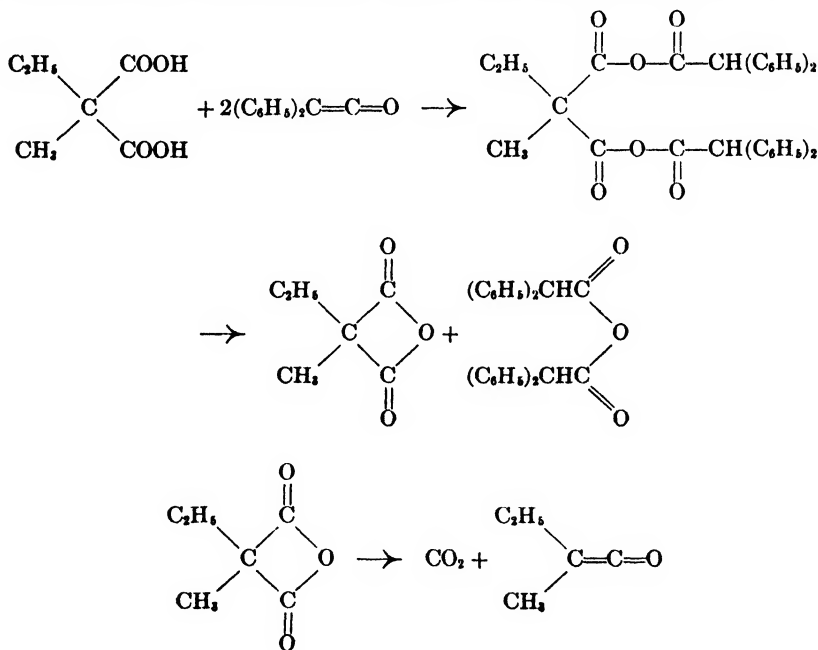
<sup>111</sup> J. Schmidlin and M. Bergman, *Ber.*, 1910, 43, 2821; *Chem. Abs.*, 1911, 5, 487. E. Berl and A. Kullman, *Ber.*, 1932, 65, 1114; *Chem. Abs.*, 1932, 26, 5067. E. Berl, German P. 536,423, 1927; *Chem. Abs.*, 1932, 26, 999. H. T. Clarke and C. E. Waring, U. S. P. 1,723,724, Aug. 6, 1929, to Eastman Kodak Co.; *Chem. Abs.*, 1929, 23, 4485. French P. 673,051, 1929, to Soc. Kodak-Pathé; *Chem. Abs.*, 1930, 24, 2474. D. A. Nightingale, U. S. P. 1,602,690, Oct. 12, 1926, to Ketoid Co.; *Brit. Chem. Abs.*, B, 1927, 28. British P. 237,573, 1924, to Ketoid Co.; *Chem. Abs.*, 1926, 20, 1415. G. H. Reid, British P. 413,709, 1934, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1935, 29, 482; see also French P. 749,245, 1933; *Chem. Abs.*, 1933, 27, 5757. J. Al, *Angew. Chem.*, 1932, 45, 545; *Chem. Abs.*, 1932, 26, 5549. C. D. Hurd and W. H. Tallin, *J.A.C.S.*, 1925, 47, 1427. C. D. Hurd, *Organic Syntheses*, 1925, IV, 39; *Chem. Abs.*, 1926, 20, 42. F. O. Rice and R. E. Vollrath, *Proc. Nat. Acad. Sci.*, 1929, 15, 702; *Brit. Chem. Abs.*, A, 192, 1425. F. O. Rice, J. Greenberg, C. E. Waters and R. E. Vollrath, *J.A.C.S.*, 1934, 56, 1760.

<sup>111</sup> C. D. Hurd, *J.A.C.S.*, 1923, 45, 3095. See also C. D. Hurd and C. Kocour, *J.A.C.S.*, 1928, 45, 2167.

workers have studied the thermal decomposition of acetic acid,<sup>118</sup> acetic anhydride,<sup>119a</sup> diacetyl and pinacolin.<sup>118</sup> Dreyfus<sup>119a</sup> found that some ketene is formed by the interaction of hydrogen and carbon monoxide at high temperatures. Staudinger and Klever<sup>114</sup> treated bromoacetyl bromide (dissolved in ether or ethyl acetate) with zinc, a current of hydrogen (or other inert gas) being conducted at the same time through the reaction vessel. Water and carbon dioxide must be excluded.

After separation of ketene from the crude products of the pyrolysis of acetic acid there were obtained (1) a fraction rich in acetone, (2) a higher-boiling liquid, which contained dimeric ketene ( $\text{CH}_3\text{COCH}=\text{CO}$ ) and dehydracetic acid, and (3) a residual brown tar.<sup>118</sup> Evaporation of the acetone fraction leaves a resinous film.<sup>118</sup>

Substituted ketenes were prepared by Staudinger<sup>117</sup> and his co-workers by treating diphenylketene with substituted malonic acids and distilling the resulting mixed anhydride. In the case of methylethylketene, reactions for its formation from diphenylketene and methylethyl malonic acid can be represented by:



This method was used in making dimethyl, diethyl, dipropyl, dibenzyl, and allylmethylketene.

The same procedure, however, could not be employed for obtaining ketenes of the allene type.<sup>119</sup> Benzalmalonyl anhydride (from silver benzalmalonate and oxalyl chloride), for example, which on distillation should yield a ketene of the

<sup>118</sup> C. D. Hurd and K. E. Martin, *J.A.C.S.*, 1929, 51, 3614.

<sup>119a</sup> E. Peytral, *Bull. soc. chim.*, 1924, 35, 960; *J.C.S.*, 1924, 126 (1), 1161. Also French P. 722,477, 1931; *Chem. Abs.*, 1932, 26, 4003.

<sup>119</sup> C. D. Hurd and W. H. Tallyn, *J.A.C.S.*, 1925, 47, 1779.

<sup>119a</sup> H. Dreyfus, *British P.* 262,364, 1925; *Brit. Chem. Abs. B*, 1927, 125.

<sup>114</sup> H. Staudinger and H. W. Klever, *Ber.*, 1908, 41, 594.

<sup>115</sup> F. Chick and N. Wilmore, *J.C.S.*, 1908, 93, 946; 1910, 97, 1987.

<sup>116</sup> E. Berl and A. Kullmann, *Ber.*, 1932, 65, 1114.

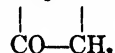
<sup>117</sup> H. Staudinger, H. Schneider, P. Schots and P. M. Strong, *Helv. Chim. Acta*, 1923, 6, 291; *Chem. Abs.*, 1923, 17, 1983.

<sup>119</sup> H. Staudinger and H. Schneider, *Helv. Chim. Acta*, 1923, 6, 316; *Chem. Abs.*, 1923, 17, 1953.



allene type,  $C_6H_5CH=C=O$ , was an amorphous, hygroscopic material which readily decomposed, even in sealed tubes, to give carbon dioxide and a resinous mass. Allene ketenes probably are not capable of existence.

Hurd and Dull<sup>119</sup> report that polymeric ketenes are produced by the thermal decomposition of substituted amides. Thus, both N-acetylcarbazole and acetylphthalimide yield the dimeric ketene (cyclobutanedione),  $CH_2-CO$ . The trimer of



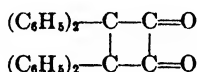
butylketene was identified as a product of the pyrolysis of caproylphthalimide. Dimers of dimethylketene and diphenylketene were obtained from iso-butyrylphthalimide and diphenylacetylphthalimide, respectively.

The linear structure for dimeric ketene (previously mentioned) is advocated by Johnson and Gross<sup>120</sup> who base their conclusions on the catalytic reduction to n-butyric acid and n-butyric anhydride.

**Polymerization of Ketenes.** According to Staudinger and Kleevers,<sup>121</sup> ketene readily polymerizes to resinous matter, though dissolved in ether (0.5-1.0 per cent solutions) it may be retained unchanged for several days. Formation of resins is accelerated by zinc or ferric chloride, sulphuric acid, and tertiary bases. No reaction occurs with oxygen, or with finely divided sodium or potassium.

Rice and Greenberg,<sup>122</sup> however, report that at room temperature polymerization of gaseous ketene is very slow, appreciable change taking place only after several hours. Although the pure liquid is stable at  $-80^\circ C$ ., transformation is rapid at  $0^\circ C$ . and is complete in about 1.5 hours. When dissolved in a solvent, reaction appears to be trimolecular. Also, there is a wide variation in the rate of polymerization in different solvents, higher values being obtained with solvents of high dielectric constants. Contrary to the results of other investigators, Rice and Greenberg report that, within their experimental error ( $\pm 20$  per cent), reaction is not inhibited by antioxidants (e.g., hydroquinone) or accelerated by acetone peroxide.<sup>123</sup> In anhydrous acetone, at  $20^\circ C$ . less than 10 per cent of the dissolved ketene is changed to diketene.<sup>124</sup>

Energetic heating of benzilic acid with anhydrous sodium carbonate yields a dimeric diphenylketene melting at  $168^\circ C$ . and considered to be 3,3,4,4-tetraphenylcyclobutane-1,2-dione,



The latter yields resinous products with a variety of reagents such as alcoholic potassium hydroxide or cyanide, phosphorus pentachloride, thionyl chloride, or acetic acid.<sup>125</sup>

Ethylbromoketene, a brownish yellow oil boiling at  $-40^\circ C$ . under 0.03 mm. pressure, quickly polymerizes on warming.<sup>126</sup> Dimethylketene reacts with isocyanates, carbon disulphide or carbon oxysulphide to give amorphous addition products of high molecular weights (3000-6000).<sup>127</sup> The latter dissolve in organic solvents yielding colloidal solutions which in many instances, after concentrating,

<sup>119</sup> C. D. Hurd and M. F. Dull, *J.A.C.S.*, 1932, 54, 2433.

<sup>120</sup> J. R. Johnson and P. F. Gross, paper presented at the New York meeting of the American Chemical Society, April, 1935.

<sup>121</sup> H. Staudinger and H. W. Kleevers, *Ber.*, 1908, 41, 594.

<sup>122</sup> F. O. Rice and J. Greenberg, *J.A.C.S.*, 1934, 56, 2132.

<sup>123</sup> C. D. Hurd, A. D. Sweet and C. L. Thomas (*J.A.C.S.*, 1933, 55, 335) report that although ketene polymerizes at  $-80^\circ C$ . it may be preserved in the presence of a trace of hydroquinone.

<sup>124</sup> British P. 410,394, 1933, to Carbide & Carbon Chemicals Corp.; *Brit. Chem. Abs.* B, 1934, 665. See also French P. 761,731, 1934; *Chem. Abs.*, 1934, 28, 4072.

<sup>125</sup> W. Langenbeck and H. Langenbeck, *Ber.*, 1928, 61, 938; *Chem. Abs.*, 1928, 22, 2746.

<sup>126</sup> H. Staudinger and H. Schneider, *Helv. Chim. Acta*, 1923, 6, 804; *Chem. Abs.*, 1923, 17, 1852.

<sup>127</sup> H. Staudinger, F. Felix and E. Geiger, *Helv. Chim. Acta*, 1925, 8, 314; *Chem. Abs.*, 1925, 19, 2189.

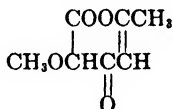
become very viscous. Dimethylketene also is converted (by trimethylamine) into a hard glassy product, which can be depolymerized on heating. This ketene yields resinous materials with aniline, or with ozone and boiling water. Heated under pressure, it forms non-uniform oily products.<sup>128</sup> Ketenes form peroxides when oxidized, and these decompose to amorphous polymers.<sup>129</sup>

The stability of alkyl ketenes appears to increase with an increase in molecular weight.<sup>130</sup> For example, at 250°C. dimethylketene polymerizes to the extent of 70 per cent in 6 hours, diethylketene 28 per cent in 20 days, and dipropylketene only 9 per cent in 28 days. Dibenzylketene, however, is less stable than the dimethyl compound, and in a few hours is completely changed into diketotetra-benzylcyclobutane. Diallylketene, on the other hand, is much more stable than the dibenzyl derivative as the former substance is polymerized 75 per cent in 5 days.

**Miscellaneous Reactions of Ketenes.** With aluminum chloride as a catalyst, ketene reacts with anisole in carbon disulphide solution forming methoxy-acetophenones and higher ketones.<sup>131</sup> Aromatic hydrocarbons may be substituted for the ether (anisole), the products from naphthalene, for example, being naphthyl methyl ketones and a dark-colored, resinous solid.

In the presence of anhydrous potassium acetate, ketene combines vigorously with benzaldehyde, nitrobenzaldehyde or furfural to give dark, viscous liquids and acid anhydrides.<sup>132</sup> With furylacrylic acid a brown liquid is obtained which polymerizes to a black jelly. Hurd, Sweet and Thomas<sup>133</sup> report that ketene and tertiary alcohols form the corresponding acetates<sup>134</sup> and with the Grignard reagent only sticky gums are secured. At -80°C. combination with isoprene was not observed. At higher temperatures von Euler and Ahlström,<sup>135</sup> however, obtained a viscous oil by this reaction.

Passage of gaseous ketene into pyridine, followed by dilution of the mixture with water, gave only a red resin and dehydracetic acid,<sup>136</sup>



Indications were that ketene does not combine with tertiary bases but merely polymerizes.<sup>137</sup> When the base is dissolved in anhydrous solvents (e.g., ether, ethyl acetate, dioxane, or a low-boiling petroleum distillate) and treated with ketene, a vigorous reaction soon occurs resulting in deposition of the resin and yellow crystals. The latter were apparently of lactone character, having the formula  $\text{C}_{18}\text{H}_{11}\text{O}_8\text{N}$ , and formed by the condensation of 4 mols of ketene and 1 mol of pyridine, with the elimination of 1 mol of water.

<sup>128</sup> H. Staudinger, F. Felix, P. Meyer and H. Harder, *Helv. Chim. Acta*, 1925, 8, 322; *Chem. Abs.*, 1925, 19, 2189.

<sup>129</sup> H. Staudinger, K. Dyckerhoff, H. Klever and L. Ruzicka, *Ber.*, 1925, 58, 1079; *Chem. Abs.*, 1925, 19, 2658.

<sup>130</sup> H. Staudinger, H. Schneider, P. Schotz and P. M. Strong, *Helv. Chim. Acta*, 1923, 6, 291; *J.C.S.*, 1923, 124, 468.

<sup>131</sup> C. D. Hurd, *J.A.C.S.*, 1925, 47, 2777.

<sup>132</sup> C. D. Hurd and C. L. Thomas, *J.A.C.S.*, 1933, 55, 275.

<sup>133</sup> C. D. Hurd, A. D. Sweet and C. L. Thomas, *J.A.C.S.*, 1933, 55, 335. Heats of reaction of ketene with aliphatic alcohols and the heat of formation of ketene were determined by F. O. Rice and J. Greenberg; *J.A.C.S.*, 1934, 56, 2270.

<sup>134</sup> For the use of ketene in acetylating alkyd resins, see M. M. Brubaker and G. De Witt Graves, U. S. P. 1,993,828, Mar. 12, 1935, to E. I. du Pont de Nemours & Co. *British P.* 419,373, 1933; *Brit. Chem. Abs. B*, 1935, 112. See also Chapter 42.

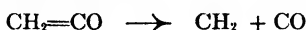
<sup>135</sup> H. von Euler and L. Ahlström, *Arkiv Kemi, Min. Geol.*, 1932, 11 (2), 1; *Chem. Abs.*, 1933, 27, 960.

<sup>136</sup> O. Wollenberg, *Ber.*, 1934, 67, 1675.

<sup>137</sup> Cf. H. Staudinger and H. W. Klever, *Ber.*, 1908, 41, 594.

In the formation of the colloidal condensation products of dimethylketene with arylcarbimides, the primary complexes, which are probably of open-chain structure, combine to form groups containing 5-10 units of the initial complexes.<sup>128</sup>

Pyrolysis of ketene has been investigated by Williamson.<sup>129</sup> At temperatures of 400-500°C. the initial reaction appeared to be the formation of the dimeric ketene ( $C_4H_4O_2$ ) followed by a slow decomposition. Above 530°C. the gaseous products were carbon monoxide (about 66 per cent), methane (30-35 per cent), and ethylene (1-3 per cent). Also a black deposit (presumably carbon) was always formed. The rates of reaction, however, did not reach their limiting values until the walls of the apparatus had been poisoned by several weeks of use. Probably initial decomposition of ketene is:



which is followed by:



At the temperatures employed, union of two methylene groups to give ethylene appeared to be of minor importance. Muller and Peytral<sup>130</sup> report that at still higher temperatures (e.g., 1150°C.) the proportion of ethylene is greater than that of methane. Also appreciable quantities of hydrogen and acetylene are found in the reaction gases.

#### RESINS FROM ARYL-ALIPHATIC KETONES

Acetophenone,  $C_6H_5COCH_3$ , yields a resin as one of the products when it is decomposed at 270-300°C. in the presence of alumina<sup>131</sup> and when it is electrolytically reduced.<sup>132</sup> The material obtained by the interaction of this ketone, phenol and hexamethylenetetramine has been employed as a binding agent.<sup>133</sup> 5-Pseudocumylacetone (from the destructive distillation of wood) decomposes slowly in the presence of alkali to yield a resin.<sup>134</sup> 1-Keto-tetra-hydrocarbazole gives an oily hydrazone and an oxime which is a glassy mass.<sup>135</sup> The phenylhydrazone of n-propyl phenyl ketone slowly changes to a resinous body on standing.<sup>136</sup>

The hydroxy ketones appear to be much less stable. For example, alkali, acid, or zinc chloride easily resinify p-hydroxybenzophenone.<sup>137</sup> Derivatives of p-methoxyacetophenone yield tarry or resinous materials when treated with acids.<sup>138</sup> Skraup and Guggenheimer<sup>139</sup> studied the effect of temperature on p-anisyl methyl, propyl, and isopropyl ketones. Only at high temperatures (340°C. for the first member of the series and 360°C. for the others) did they undergo loss of water and autocondensation, followed by the rapid occurrence of resinification and carbonization products.

$\alpha$ -Chloroacetophenone and  $\beta$ -chloropropiophenone, when treated with sodium in liquid ammonia, are transformed to hard, chlorine-free resins.<sup>140</sup> Substances of

<sup>128</sup> E. Geiger, *Gummi-Ztg.*, 1926, 40, 2143; *Brit. Chem. Abs. B*, 1926, 681.

<sup>129</sup> A. T. Williamson, *J.A.C.S.*, 1934, 56, 2216.

<sup>130</sup> J. A. Muller and E. Peytral, *Compt. rend.*, 1933, 196, 279; *Chem. Abs.*, 1933, 27, 1864.

<sup>131</sup> W. Ipatiev and W. Petrov, *Ber.*, 1927, 60, 1956.

<sup>132</sup> S. Swann, Jr. and G. H. Nelson, *Trans. Electrochem. Soc.*, 1935, 67, 49; *Brit. Chem. Abs. A*, 1935, 176. See also the reduction of a racemic hydrogenated chrysene diketone, J. v. Braun and G. Irmisch, *Ber.*, 1931, 64, 2461; *Chem. Abs.*, 1932, 26, 463.

<sup>133</sup> British P. 9,292, 1914, to S. Karpen & Bros.; *J.S.C.I.*, 1915 34, 628.

<sup>134</sup> J. B. Holmberg, *Svensk. Kem. Tid.*, 1928, 40, 304; *Brit. Chem. Abs. B*, 1929, 158.

<sup>135</sup> S. Coffey, *Rec. trav. chim.*, 1923, 42, 528; *Chem. Abs.*, 1923, 17, 3493.

<sup>136</sup> R. Sorge, *Ber.*, 1902, 35, 1065.

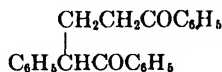
<sup>137</sup> W. T. Minaev, *J. Russ. Phys.-Chem. Soc.*, 1926, 58, 307; *Brit. Chem. Abs. A*, 1927, 361.

<sup>138</sup> M. T. Bogert and L. P. Curtin, *J.A.C.S.*, 1923, 45, 2161.

<sup>139</sup> S. Skraup and S. Guggenheimer, *Ber.*, 1925, 58, 2488.

<sup>140</sup> P. Dean and G. Berchet, *J.A.C.S.*, 1930, 52, 2823.

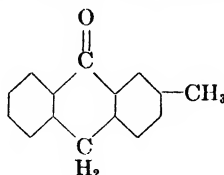
a resinous nature are obtained by heating di-(bromobenzoyl)-ethanol (an orange-colored solid melting at 102°C.) dissolved in an organic solvent<sup>151</sup> or by bromination of 1,2,5-triphenylpentanedione-1,5,<sup>152</sup>



The dibromide of this diketone gives an intractable resin when treated with potassium acetate.

Tetrabenzoyl ethylene<sup>153</sup> and also dibenzoyl,<sup>154</sup>  $\text{C}_6\text{H}_5\text{CO}-\text{OCC}_6\text{H}_5$ , undergo condensation on exposure to light. About 50 per cent of the latter ketone, in 66 per cent solution in alcohol, is converted into resinous bodies after 12 hours exposure. Cinnamylidene-m-nitroacetophenone, in chloroform solution, is readily transformed in sunlight to a colophony-like substance melting between 65° and 70°C., although cinnamylidene-acetophenone is much less affected under the same conditions. Apparently, in aromatic compounds the nitro (and acetamino) group favors resin-formation.<sup>155</sup> Methoxybenzal-acetophenone<sup>156</sup> and 4,4-di-(hydroxymethyl)-benzophenone<sup>157</sup> are resinified by light. The dichloro compound of the latter, dihydroxy-ketone, (in alcohol solution) and ammonia at 80°C. yielded a polymer in which at least 10 mols were combined.

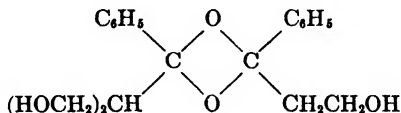
Reaction of methyl magnesium iodide, or solutions of the Grignard reagent, with phenylacetylnaphthalene,<sup>158</sup>  $\text{C}_{10}\text{H}_7\text{COCH}_2\text{C}_6\text{H}_5$ , or with 2-methyl-9-anthrone,<sup>159</sup>



gives resinous masses.

#### CONDENSATION OF ARYL-ALIPHATIC KETONES WITH ALDEHYDES

Acetophenone and formaldehyde combine, in the presence of ammonium chloride, to give two compounds, monomethylolacetophenone,  $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{OH}$ , and trimethylol-bisacetophenone,



The former derivative on dehydration and the latter on steam distillation give an oil (phenyl vinyl ketone,  $\text{C}_6\text{H}_5\text{COCH}=\text{CH}_2$ ) which sets to an extremely hard,

<sup>151</sup> R. Sutz, *J.A.C.S.*, 1926, 48, 2905.

<sup>152</sup> C. Allen and W. Barker, *J.A.C.S.*, 1932, 54, 736.

<sup>153</sup> H. von Halban and R. Rast, *Z. physik. Chem., Bodenstern Festband*, 1931, 303; *Brit. Chem. Abs.* A, 1931, 1295.

<sup>154</sup> C. Porter, H. Ramsperger and C. Steel, *J.A.C.S.*, 1923, 45, 1827. H. Gelissen and P. H. Hermans (*Ber.*, 1925, 58, 770) report that dibenzoyl peroxide and glacial acetic acid react to form a yellow, sticky resin which becomes glassy upon distillation *in vacuo*.

<sup>155</sup> M. Giua, *Gazz. chim. ital.*, 1925, 55, 567; *Chem. Abs.*, 1926, 20, 749. See also M. Giua and E. Bagella, *Gazz. chim. ital.*, 1921, 51 (2), 116; *Chem. Abs.*, 1922, 16, 557.

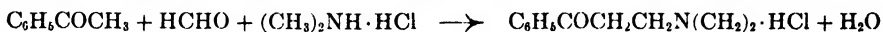
<sup>156</sup> C. Dufraisse and R. Chauv, *Bull. soc. chim.*, 1926, 39, 443; *Chem. Abs.*, 1926, 20, 2156.

<sup>157</sup> E. Connerade, *Bull. soc. chim. Belg.*, 1933, 42, 311; *Brit. Chem. Abs.* A, 1933, 1051.

<sup>158</sup> J. W. Cook and R. A. E. Galley, *J.C.S.*, 1931, 2012.

<sup>159</sup> E. deB. Barnett and N. F. Goodway, *J.C.S.*, 1929, 1754.

gummy mass in a few days.<sup>100</sup> Substitution of methylamine hydrochloride for ammonium chloride results in the formation of two compounds,  $\alpha, \alpha'$ -bisphenacyl-methylmethylamine,  $(C_6H_5COCH_2CH_2)_2NCH_3$ , and  $\alpha$ -methylaminopropiophenone,  $C_6H_5COCH_2CH_2NHCH_3$ .<sup>101</sup> When dimethylamine hydrochloride is employed as the condensing agent  $\omega$ -dimethylaminopropiophenone hydrochloride is obtained.



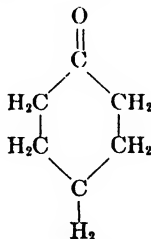
The latter compound is easily hydrolyzed (with steam) to dimethylamine and phenyl vinyl ketone. Allen and Bridgess<sup>102</sup> found that addition of alcohol to phenyl vinyl ketone, prepared in this manner, caused the deposition of a white, insoluble mass of polymeric material.

Condensation under alkaline conditions often furnishes resins. For example, acetophenone, formaldehyde and potassium hydroxide yield an infusible, elastic, pale resinous product which is soluble in carbon tetrachloride, acetone, and ethyl acetate.<sup>103</sup> Similar results were obtained with propionylacetone or butyrylacetophenone and salicylic aldehyde<sup>104</sup> (with piperidine), and this same aldehyde and acetylbenzoyl<sup>105</sup> (with aniline). On the other hand, Dufraisse and Demontrignier<sup>106</sup> effected reaction of acetophenone with acetaldehyde by means of sodium ethoxide. The product, after treatment with zinc chloride, gave 2-methylvinyl phenyl ketone ( $C_6H_5COCH=CHCH_3$ , m.p.  $20^\circ C.$ ) which was much more stable than its lower homologue.

4,4'- or 2,4'-Dihydroxybenzophenone condenses with aldehydes, in the presence of hydrochloric acid, forming resinous products which are compatible with cellulose acetate.<sup>107</sup> Polycarboxylic acids of diaryl ketones furnish varnish resins when heated with rosin and glycerol.<sup>108</sup> Reduction of mono- and dimethylantrones results in the production of colored polymers which greatly reduces the yield of bianthrone.<sup>109</sup>

### CYCLIC KETONES

Cyclohexanone, a typical cyclic ketone, boils at  $155^\circ C.$ , is slightly soluble in



water and has an odor similar to peppermint. Although it can be prepared by the dry distillation of calcium pimelate it is usually made by dehydrogenation of cyclohexanol.

Resinification of cyclic ketones has been shown to follow a course similar to that of acetone. For example cyclohexanone, when heated at  $320^\circ C.$  under 30

<sup>100</sup> C. van Marle and B. Tollens, *Ber.*, 1903, 36, 1351.

<sup>101</sup> C. Mannich and G. Heilner, *Ber.*, 1922, 55, 356.

<sup>102</sup> C. Allen and M. Bridgess, *J.A.C.S.*, 1929, 51, 2151.

<sup>103</sup> German P. 402,996, 1921, to A.-G. für Anilin-Fabr.; *J.S.C.I.*, 1925, 44, 216B.

<sup>104</sup> A. B. Lovett and E. Roberts, *J.C.S.*, 1928, 1976.

<sup>105</sup> W. Borsche and J. C. Titsingh, *Ber.*, 1909, 42, 4283.

<sup>106</sup> C. Dufraisse and M. Demontrignier, *Bull. soc. chim.*, 1927, 41, 843; *Chem. Abs.*, 1927, 21, 3901.

<sup>107</sup> British P. 376,839, 1930, to British Celanese, Ltd.; *Brit. Chem. Abs.* B, 1932, 948.

<sup>108</sup> H. A. Bruson, U. S. P. 1,829,038, Oct. 27, 1931, to Röhm & Haas Co.; *Chem. Abs.*, 1932, 26, 861.

<sup>109</sup> E. Barnett, *Ber.*, 1932, 65, 1563.

atmospheres pressure with alumina, gives mono- and dicyclohexylidene-cyclohexanones and dodecahydrotriphenylene, the analogues of mesityl oxide, phorone and mesitylene, respectively.<sup>170</sup> The same products were obtained by Cornubert<sup>171</sup> by treating cyclohexanone with sodamide. Cyclohexanone condenses with a methyl alcohol-sulphuric acid mixture to form an oil, which on distillation at 18 mm. pressure was found to contain about 30 per cent of resin.<sup>172</sup> By heating cyclohexanone or its homologues with methyl-alcoholic potassium hydroxide under pressure at about 200°C., a brown, oil-soluble varnish resin is obtained. Cyclohexylidene-cyclohexanone forms an almost colorless resin at 120°C. in the presence of a small quantity of alkaline<sup>173</sup> or acid<sup>174</sup> condensing agents.

Light-colored resins, unaffected by sunlight and unattacked by acids or alkalies, are formed when cyclohexanone is condensed alone or with cyclohexanol by boiling with alcoholic potassium hydroxide.<sup>175</sup> Steam distillation removes uncondensed material; water-washing removes the catalyst. The purified product is a hard, clear resin, soluble in most organic solvents, particularly benzene and oils, and is compatible with cellulose esters and rubber.

Methylcyclohexanone reacts with sorbitol to form an acetal.<sup>176</sup> Finkelstein<sup>177</sup> incorporated a cyclic ketone resin with nitrocellulose of low viscosity in a solvent mixture containing ethyleneglycol methyl ether, ethyleneglycol butyl ether, and ethyl alcohol to make a brushing lacquer.<sup>178</sup>

Cyclopropanone exists as a monomer only in solution; and its hydrate, 1,1-dihydroxycyclopropane, forms resinous polymeric material when an ether solution of it is evaporated in the absence of moisture.<sup>179</sup> Oxidation of cyclopentadecanone yields an open-chain acid, lactones and resinous products.<sup>180</sup>

The elimination of hydrogen bromide from 2-bromo-2-methyl-1-hydrindone (with pyridine) gives 2-methyl-1-indone, a solid melting at 47-47.5°C. and boiling at 99-100°C. at 6 mm. pressure.<sup>181</sup> It polymerizes readily when heated to its boiling temperature (240°C.) at atmospheric pressure, and less quickly on warming with alcoholic sodium or potassium hydroxide. When stored, 2-methyl-1-indone slowly changes to a yellow glassy solid. Similarly, 2-hydrindone slowly undergoes decomposition yielding resinous products.<sup>182</sup> Methylenehydrindone<sup>183</sup> resinifies on standing to either a gelatinous product or a white powder, which is apparently a polymer containing 12 molecules. At temperatures above 400°C., the more complex ketones, camphor and fenchone, undergo pyrolysis and form ill-defined, polymerized, unsaturated compounds.<sup>184</sup>

Absorption of oxygen by carvone, piperitone, pulegone, p-benzoquinone, phenanthrenequinone and  $\beta$ -naphthoquinone in the presence of alcohol and barium

<sup>170</sup> A. Petrov, *Bull. soc. chim.*, 1928, 43, 1272; *Chem. Abs.*, 1929, 23, 4453

<sup>171</sup> R. Cornubert, *Compt. rend.*, 1927, 184, 1253; *Chem. Abs.*, 1927, 21, 1464.

<sup>172</sup> K. Kunze, *Ber.*, 1926, 59, 2086; *Brit. Chem. Abs. A*, 1926, 1143.

<sup>173</sup> German P. 337,993, 1919, to Badische Anilin- & Soda-Fabrik; *J.S.C.I.*, 1921, 40, 631A. British P. 146,498, 1920; *J.S.C.I.*, 1921, 40, 781A. Swiss P. 89,060, 1920.

<sup>174</sup> British P. 170,361, 1920, addn. to 146,498, to Badische Anilin- & Soda-Fabrik; *J.S.C.I.*, 1922, 41, 22A.

<sup>175</sup> O. Schmidt, K. Seydel and N. Roh, U. S. P. 1,823,127, Sept. 15, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 325. British P. 276,518, 1926; *Chem. Abs.*, 1928, 22, 2475. German P. 511,092, 1925; *Chem. Zentr.*, 1931, 1, 2123.

<sup>176</sup> G. Kränzlein, E. Dickhauser and A. Voss, U. S. P. 1,902,866, Mar. 28, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3223.

<sup>177</sup> H. Finkelstein, U. S. P. 1,818,547, Aug. 11, 1931, and 1,900,700, Mar. 7, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 5584; 1933, 27, 3093.

<sup>178</sup> See also G. Steimmig, U. S. P. 1,864,099, June 21, 1932, and O. Jordan, U. S. P. 1,865,191, June 28, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4487. British P. 304,814, 1927; *Brit. Chem. Abs. B*, 1929, 320.

<sup>179</sup> P. Lipp, U. Buchkremer and H. Seoles, *Ann.*, 1932, 449, 1; *Brit. Chem. Abs. A*, 1932, 1249.

<sup>180</sup> L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1928, 11, 1159; *Brit. Chem. Abs. A*, 1929, 68.

<sup>181</sup> N. Kishner, *J. Gen. Chem. (U. S. S. R.)*, 1933, 3, 201; *Chem. Abs.*, 1934, 28, 1692.

<sup>182</sup> L. S. Walters, *J.S.C.I.*, 1927, 46, 150T.

<sup>183</sup> H. Rupe and W. Wieland, *Helv. Chim. Acta*, 1926, 9, 1001; *Brit. Chem. Abs. A*, 1927, 58.

<sup>184</sup> W. Treibs, *Ber.*, 1928, 61, 683; *Chem. Abs.*, 1928, 22, 2148.

hydroxide, furnishes brown resinous materials.<sup>185</sup> Sudden polymerization occurs when concentrated acid solutions of reductone are heated above 100°C. The product is viscous and amorphous.<sup>186</sup>

**Condensation of Cyclic Ketones with Aldehydes.** From the condensation of cyclopentanone with a large excess of aqueous formaldehyde in the presence of lime, Mannich and Brose<sup>187</sup> obtained amorphous products. On decreasing the proportion of aldehyde, the tetramethylol derivative was formed. For example, 20 g. of cyclohexanone, 315 g. of 9 per cent aqueous formaldehyde and 10 g. of lime gave 17 g. of tetramethylol-cyclohexanol. Equimolecular proportions of ketone and formaldehyde yielded the monomethylol derivative, a liquid boiling at 114°C. under 16 mm. pressure, unstable to both acids and alkalis. Neither menthone, carvone nor camphor could be condensed with formaldehyde.<sup>188</sup>

Cyclic ketones and aldehydes yield resins when condensed in acid or alkaline media. For example, a transparent and almost odorless and colorless product is obtained by refluxing 100 parts of cyclohexanone, 110 parts of 30 per cent aqueous formaldehyde, and 3 parts of concentrated caustic soda solution.<sup>189</sup> Seydel<sup>190</sup> suggests effecting reaction at higher temperatures (150-200°C.) and under pressure. Incorporation of rosin with cyclohexanone, cresylic acid, and formaldehyde gives a varnish resin.<sup>191</sup>

Norton and Sontag<sup>192</sup> point out that soluble and fusible resins are produced when mild alkalis are employed, and insoluble, infusible resins when strong alkalis are used. Sodium carbonate or borate is suggested as the alkaline condensing agent. The reaction products are said to be light-colored or white, and do not darken on exposure to rays from a mercury arc lamp. For example, 100 parts of cyclopentanone, 125 parts of formalin and 4 parts of sodium borate are refluxed at 100°C. until a syrupy liquid is obtained. The latter can be dehydrated to a permanently fusible resin.

The resins from cyclic ketones are resistant to alkali and to acid and are compatible with cellulose derivatives and rubber. Twiss and Jones<sup>193</sup> treated rubber, cyclohexanone, and formaldehyde (in a solvent) with hydrogen chloride to obtain a material for bonding rubber to metals. Steimmig<sup>194</sup> described the preparation of a brushing lacquer by incorporating a cyclohexanone-phenol-formaldehyde resin with low viscosity nitrocellulose and solvents. Moldable material is secured by reacting cyclohexanone with a partially formed phenol-formaldehyde resin.<sup>195</sup> Dreyfus<sup>196</sup> made resins, which may be used in lacquers, by refluxing cyclohexanone with acetaldehyde in alcoholic caustic soda.

<sup>185</sup> W. Treibs, *Ber.*, 1930, 63, 2423; *Chem. Abs.*, 1931, 25, 938. See also *Ber.*, 1931, 64, 2178, 2545; 1933, 66, 610.

<sup>186</sup> H. von Euler and C. Martius, *Ann.*, 1933, 505, 73; *Brit. Chem. Abs. A.*, 1933, 937.

<sup>187</sup> C. Mannich and W. Brose, *Ber.*, 1923, 56, 833; *Chem. Abs.*, 1923, 17, 2704.

<sup>188</sup> For the reaction of various cyclohexanone and cyclopentanone derivatives with benzaldehyde, see I. R. Cornubert and C. Borrel, *Bull. soc. chim.*, 1929, (4) 45, 1148; *Chem. Abs.*, 1930, 24, 2730; *Bull. soc. chim.*, 1930, (4) 47, 301; *Chem. Abs.*, 1930, 24, 3997; *Bull. soc. chim.*, 1930 (4) 47, 988; *Chem. Abs.*, 1931, 25, 508; *Bull. soc. chim.*, 1931 (4) 49, 1229; *Chem. Abs.*, 1932, 26, 701.

<sup>189</sup> German P. 339,107, 1918, to Badische Anilin- & Soda-Fabrik; *J.C.S.I.*, 1921, 40, 742A. See also J. Baer and G. Baer, Swiss P. 149,429, 1929; *Chem. Abs.*, 1932, 26, 4970.

<sup>190</sup> K. Seydel, German P. 403,646, 1922, to Badische Anilin- & Soda-Fabrik; *J.S.C.I.*, 1925, 44, 217B.

<sup>191</sup> O. Schmidt and K. Seydel, German P. 420,414, 1925, to Badische Anilin- & Soda-Fabrik; *Chem. Zentr.*, 1926, 1, 1800.

<sup>192</sup> A. J. Norton and L. Sontag, U. S. P. 1,985,870, Dec. 25, 1934, to General Plastics, Inc.; *Chem. Abs.*, 1935, 29, 1176.

<sup>193</sup> D. F. Twiss and F. A. Jones, U. S. P. 1,915,808, June 27, 1933, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 4717. British P. 348,303, 1930; *Brit. Chem. Abs. B.*, 1931, 731. See also O. A. Thompson, British P. 388,776, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 5909. O. Schmidt and K. Seydel, German P. 508,994, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 835.

<sup>194</sup> G. Steimmig, U. S. P. 1,883,060, Oct. 18, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 837.

<sup>195</sup> K. A. Schuch, German P. 567,072, 1930, to A. Nowack A.-G.; *Chem. Abs.*, 1933, 27, 1464.

<sup>196</sup> H. Dreyfus, British P. 181,575, 1931; *J.S.C.I.*, 1932, 41, 600A.

Polymerized cyclohexanone or cyclohexanone-formaldehyde resins may be employed in the manufacture of electrical insulators,<sup>197</sup> or mixed with castor oil and chalk, serve as compounds to seal joint boxes in electrical wiring systems.<sup>198</sup> Pigments may be incorporated with the latter composition.

#### MISCELLANEOUS RESINS

5-Phenyl-3-methylcyclohexanone yields a dibromide which becomes tarry at atmospheric temperature.<sup>199</sup> A similar reaction is observed in the case of dibenzilidene-cyclohexylidenecyclohexanone.<sup>200</sup> Bromine, acetyl chloride and thionyl chloride react with cyclohexanonebenzil to give yellow gums.<sup>201</sup> 1-Phenyl-4-ethylcyclohexane-3,5-dione absorbs oxygen from the air and becomes resinous.<sup>202</sup> When boiled for 36 hours with aqueous potassium hydroxide, cyclohexenylacetone gives a quantity of gummy substances.<sup>203</sup>

By condensation of cyclohexylidene-cyclohexanone and terephthalaldehyde in the presence of alkali, Kunze<sup>204</sup> obtained a bright yellow, amorphous powder which decomposed at high temperatures without melting.

The reaction products of acetone or cyclohexanone with glycerol are said to be soft and pliable and may be used as plasticizers for cellulose ethers or esters.<sup>205</sup> Cyclohexanone and phenol (in benzene solution) in the presence of hydrogen chloride give diphenylol-1,1-cyclohexane which in turn is converted by the halogen acid into a resin melting at 200°C.<sup>206</sup> The cyclic ketone condenses also with polymeric vinyl alcohol<sup>207</sup> and with resorcinol.<sup>208</sup>

Ngaiol, a secondary alcohol obtained by reduction of ngaione ( $C_{15}H_{22}O_3$ , an oxygenated sesquiterpene ketone) completely resinifies at 0°C. when treated with 80 per cent sulphuric acid or 100 per cent formic acid. Complete saturation of ngaiol with hydrogen results in the formation of a colorless, viscous oil. A mixture of ngaiol and potassium hydrogen sulphate heated at 190°C. in an atmosphere of carbon dioxide yields dehydrongiene dioxide which rapidly absorbs oxygen from the air and forms a thick brown oil.<sup>209</sup>

Tropinonemonocarboxylic esters are obtained by the condensation of succinic aldehyde, methylamine and acetoacetic esters. On purification they exhibit the properties of drying oils.<sup>210</sup>

The reaction of aromatic ketones or ethers with acetic anhydride and sulphuric acid yields pyrillium (oxonium) compounds which may be isolated as their salts of perchloric acid.<sup>210a</sup> Acetophenone, for example, gives 2,6-diphenyl-4-methylpyrillium perchlorate,

<sup>197</sup> H. Rost, British P. 408,225, 1934; *Chem. Abs.*, 1934, 28, 5555.

<sup>198</sup> H. A. Tunstall and F. G. R. Jesson, British P. 409,672, 1934, to W. T. Henleys Telegraph Co. Ltd.; *Chem. Abs.*, 1934, 28, 6357.

<sup>199</sup> A. Petrov, *Ber.*, 1930, 63, 898. See also R. S. Thakur, *J.C.S.*, 1933, 1477.

<sup>200</sup> K. Kunze, *Ber.*, 1926, 59, 2087.

<sup>201</sup> C. F. H. Allen, *Can. J. Research*, 1931, 4, 264; *Brit. Chem. Abs. A*, 1931, 845.

<sup>202</sup> I. Mattar, J. Hastings and T. Walker, *J.C.S.*, 1930, 2455.

<sup>203</sup> M. D. Farrow and G. A. R. Kon, *J.C.S.*, 1926, 2138.

<sup>204</sup> K. Kunze, *Ber.*, 1926, 59, 2087.

<sup>205</sup> French P. 589,732, 1926, to Soc. chim. des usines du Rhone; *Plastics*, 1926, 2, 206.

<sup>206</sup> K. Seydel and N. H. Roh, German P. 484,739, to I. G. Farbenind. A.-G.

<sup>207</sup> G. Kramstein, A. Voss and W. Starck, U. S. P. 1,933,966, Nov. 7, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 664.

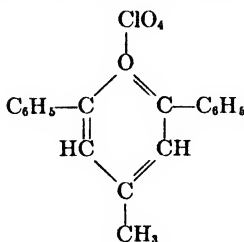
<sup>208</sup> British P. 368,801, 1930, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1932, 475.

<sup>209</sup> F. H. McDowall, *J.C.S.*, 1927, 731.

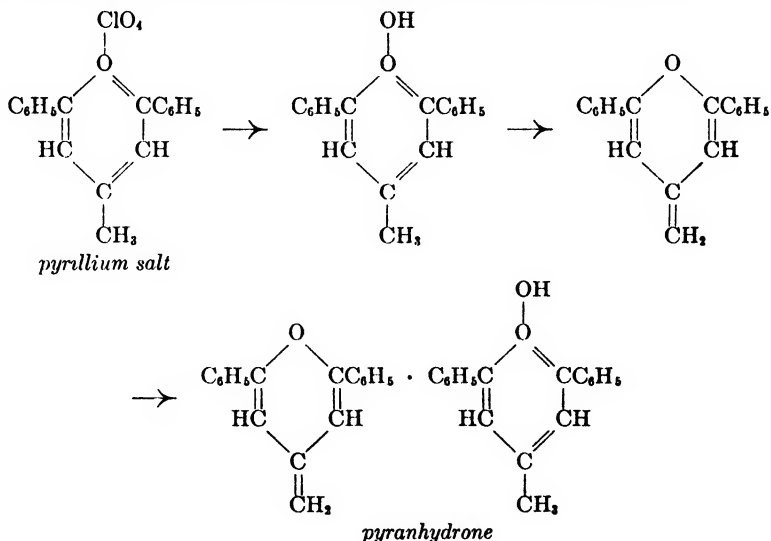
<sup>210</sup> R. Willetätter, O. Wolfes and H. Maeder, U. S. P. 1,419,091, June 6, 1923; *J.S.C.I.*, 1922, 41, 567A. O. Wolfes and H. Maeder, U. S. P. 1,419,092, June 6, 1923; *J.S.C.I.*, 1922, 41, 567A. German P. 344,031, 1919, to E. Merck Chem. Fabr.; *J.S.C.I.*, 1922, 41, 270A. E. Merck and O. Wolfes, British P. 153,917, 1920; *J.S.C.I.*, 1922, 41, 436A.

<sup>210a</sup> W. Schneider and H. F. W. Meyer, *Ber.*, 1921, 54, 1484.





With mildly alkaline solutions (e.g., sodium acetate) this is converted into the oxonium base, which in turn loses a molecule of water and changes to  $\gamma$ -methylene-pyran. The latter forms a colored quinhydrone-like addition compound with the oxonium base for which the term pyranhydrone has been suggested.



When the pyranhydrone (derived from acetophenone) is heated *in vacuo* at 125°C. a molecule of water is lost and a brownish-black glassy material obtained.

Intensive drying of triquinoyl hydrate,  $C_6O_5 \cdot H_2O$ , at 76°C. results in the formation of a yellowish-brown material which may be regarded as polymeric carbon monoxide,  $(C_6O)_x$ .<sup>211</sup> Benzo- and toluquinones (in alcohol solutions) with phenylhydrazine furnish oily liquids insoluble in water.<sup>212</sup> With quinone and ammonia (in ether) brown, amorphous substances are procured.<sup>213</sup>

#### ARYLIDENE KETONES

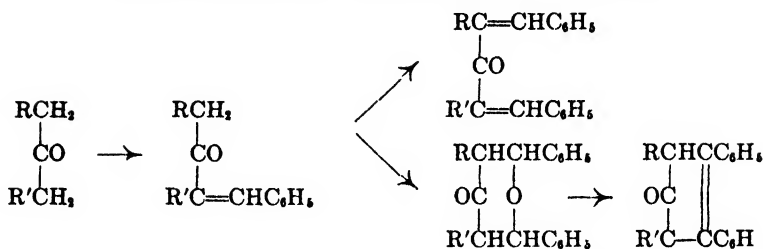
Benzaldehyde and an aliphatic ketone yield, in the simplest case, a benzylidene ketone. When the ketone carries two methylene groups adjacent to the carbonyl, a dibenzylidene compound can be formed, which by dehydration is transformed into cyclopentenone derivatives.<sup>214</sup>

<sup>211</sup> F. Bergel, *Ber.*, 1929, 62, 490.

<sup>212</sup> T. Zincke, *Ber.*, 1883, 16, 1563.

<sup>213</sup> T. Zincke, *Ber.*, 1883, 16, 1555.

<sup>214</sup> H. Ryan and P. J. Cahill, *Proc. Roy. Irish Acad.*, 1924, 36B, 334; *Chem. Abs.*, 1925, 19, 467. H. Ryan and J. J. Lennon, *ibid.*, 1925, 37B, 27; *Chem. Abs.*, 1925, 19, 2934. F. R. Japp and W. Maitland, *J.C.S.*, 1904, 85, 1488. D. Vorländer and K. Hobohm, *Ber.*, 1896, 29, 1352. D. Vorländer, *Ber.*, 1897, 30, 2262.



Of the arylidene derivatives of acetone, monobenzylideneacetone yields a resinous product when heated at 230°C. for 12 hours with sodium phenoxide or ethoxide.<sup>215</sup> Sunlight resinifies dibenzylideneacetone in alcoholic solution. Exposure for several months effected 80 per cent conversion to a white powder melting at 125-135°C. and having an approximate composition of  $(\text{C}_{17}\text{H}_{16}\text{O})_x$ .<sup>216</sup> Other methods for converting dibenzylideneacetone into colored polymers of high molecular weights and high melting points include treatment with concentrated alkaline solutions and heating at 180°C. in a stream of carbon dioxide.<sup>217</sup> The resin from the latter procedure was reddish brown, melting at 85-90°C., was soluble in benzene, chloroform, ether, tetrahydronaphthalene, acetone, ethyl acetate and glacial acetic acid, moderately soluble in turpentine and fatty oils, but insoluble in alcohol and petroleum ether. Lacquers made from it in volatile solvents were of good quality. Efforts to produce the resin by heating the ketone in a solvent boiling at a high temperature (for example, decahydronaphthalene, boiling point 185-195°C.) did not give satisfactory results.<sup>218</sup>

An investigation of the effect of heat on several mono- and di-arylidene ketones showed that the grouping  $-\text{CH}=\text{CHCO}-$  was responsible for resinification; that is, this group is a "resinophore."<sup>219</sup> It was noted also that the rate of reaction was a linear function of the number of double bonds, or olefin linkages, in the molecule. In marked contrast, however, the spontaneous polymerization of methyleneacetone,  $\text{CH}_2=\text{CHCOCH}_3$ , and phenyl vinyl ketone,  $\text{C}_6\text{H}_5\text{COCH}=\text{CH}_2$ , indicates that the grouping  $\text{CH}_2=\text{CHCO}-$  is the more reactive resinophore. Although methyleneacetone,  $(\text{CH}_3)_2\text{CH}_2=\text{CCOCH}_3$ , polymerizes more slowly than methyleneacetone, the isomeric ethylideneacetone,  $\text{CH}_3\text{CH}=\text{CHCOCH}_3$ , is not known to polymerize spontaneously, and mesityl oxide,  $(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$ , and phorone  $(\text{CH}_3)_2\text{C}=\text{CHCOCH}=\text{C}(\text{CH}_3)_2$ , are equally stable. With this in mind, one does not wonder at the instability of the ketenes,  $\text{CO}=\text{CR}'\text{R}$ .

Kreidl<sup>220</sup> prepared varnish resins by heating compounds of the formula  $\text{R}(\text{CH}=\text{CH})_n\text{COR}''$  or  $\text{R}(\text{CH}=\text{CH})_n\text{CO}(\text{CH}=\text{CH})_m\text{R}'$  (where R and R' are aryl and R'' may be aryl or alkyl and n is 1 or 2) for several hours above their melting point. Dicinnylideneacetone forms a resin melting at 130-145°C.; anisalcinnylideneacetone, 135-140°C.; anisalacetone 50-60°C.; and cinnamylideneacetone 55-70°C. The products are soluble in many of the organic solvents with the exception of petroleum hydrocarbons, slightly soluble in alcohol, and fairly soluble in turpentine and fatty oils. The evaporated solutions yield adherent, durable films, stable to light, air, and water.

Styryl ketones,  $\text{C}_6\text{H}_5\text{CH}=\text{CHCOR}$ , exist in both mono- and dimeric forms.

<sup>215</sup> S. Ruhemann, *J.C.S.*, 1909, 95, 111. See also W. Borsche, *Ber.*, 1909, 42, 4496; *Chem. Abs.*, 1910, 4, 590.

<sup>216</sup> G. Ciamician and P. Silber, *Ber.*, 1909, 42, 1359; *Chem. Abs.*, 1909, 3, 2294. See also P. Praetorius and F. Korn, *Ber.*, 1910, 43, 2744; *Chem. Abs.*, 1911, 5, 484.

<sup>217</sup> I. J. Postovski and B. P. Lugovkin, *J. Gen. Chem. Russ.*, 1930, 1, 1006; *Brit. Chem. Abs. A.*, 1932, 618.

<sup>218</sup> W. Herzog and J. Kreidl, *Z. angew. Chem.*, 1922, 35, 465, 641; *Chem. Abs.*, 1923, 17, 1339, 1732.

<sup>219</sup> See Chapter 4.

<sup>220</sup> I. Kreidl, German P. 397,803, 1922; *J.S.C.I.*, 1924, 43, 879B.

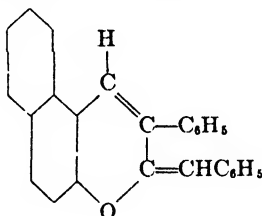
The latter are postulated as cyclobutane derivatives of truxillic and truxinic ketones.<sup>221</sup> Alcoholic solutions of phenyl o- and p-methoxystyryl ketones resinify either in sunlight or in the presence of acid.

**Miscellaneous Reactions of Arylidene Ketones.** Styryl methyl ketones readily condense with chloroaldehydes in the presence of sodium ethoxide to give amorphous polymers.<sup>222</sup> In an attempt to prepare m-hydroxystyryl methyl ketone from m-hydroxybenzaldehyde and acetone, McGookin and Sinclair<sup>223</sup> isolated only a dark brown, amorphous substance. Electrolytic reduction of styryl methyl ketone in alcoholic caustic soda solution, with a mercury cathode yielded some resin, and with other cathode materials dimeric substances were obtained.<sup>224</sup>

Exposure to light effects resinification of the double compound of dibenzilidene and stannic chloride, of methyl ketopentadienecarboxylate,<sup>225</sup> and cinnamylideneacetylacetone.<sup>226</sup> Cinnamylideneacetone polymerizes even in the dark in the presence of air but more rapidly under the influence of light. Its dimer is a colorless solid, which by the action of heat forms a resinous trimer.

3,4-Dimethoxy- and 3-methoxy-4-ethoxy-styryl methyl ketones were converted almost completely into resins by heating with piperidine.<sup>227</sup> With an acetone-alcohol solution of 3-methoxy-4-isopropoxy-styryl methyl ketone, reaction occurred even in the cold. The formation of polymers was observed when cinnamic aldehyde combined with either acetone or cyclohexanone in presence of caustic soda.<sup>228</sup>

Benzoyl- and acetylacetones condense with anisaldehyde and m-nitrobenzaldehyde, in the presence of piperidine, to yield resins.<sup>229</sup> In a similar manner, 2-naphthol-1-aldehyde and dibenzylketone form 2-benzylidene-3-phenyl- $\Delta^8$ - $\beta$ -naphthpyran,



In acetone solution this compound polymerizes after several days.<sup>230</sup>

<sup>221</sup> I. M. Heilbron and F. Irving, *J.C.S.*, 1928, 2323; 1929, 931. H. Stobbe and A. Hensel, *Ber.*, 1926, 59, 2254; *Chem. Abs.*, 1927, 21, 396.

<sup>222</sup> I. M. Heilbron and R. Hill, *J.C.S.*, 1928, 2864.

<sup>223</sup> A. McGookin and D. J. Sinclair, *J.C.S.*, 1928, 1174.

<sup>224</sup> G. Shima, *Mem. Coll. Sci. Kyoto*, 1929, 12, 327; *Brit. Chem. Abs. A*, 1930, 344.

<sup>225</sup> H. Stobbe and E. Färber, *Ber.*, 1925, 58, 1548; *Chem. Abs.*, 1926, 20, 180.

<sup>226</sup> H. Stobbe, A. Hensel and W. Simon, *J. prakt. Chem.*, 1925, 110, 129; *Chem. Abs.*, 1925, 19, 2941.

<sup>227</sup> R. Dickinson, I. Heilbron and F. Irving, *J.C.S.*, 1927, 1891.

<sup>228</sup> D. Vorländer, E. Fischer and E. Kunze, *Ber.*, 1925, 52, 1284.

<sup>229</sup> W. Diltthey and H. Steinborn, *J. prakt. Chem.*, 1932, 133, 219; *Chem. Abs.*, 1932, 26, 2974.

<sup>230</sup> R. Dickinson, I. M. Heilbron and F. O'Brien, *J.C.S.*, 1928, 2078.

## Chapter 26

### Urea-Formaldehyde Resins. Historical. Theoretical

The two outstanding series of moldable resins are unquestionably phenol-formaldehyde and urea-formaldehyde, for they possess in common many valuable properties denied to any other group of substances. The most distinguishing property is the characteristic ability of these resins to cure rapidly. It has been shown in the previous chapters that the rapid-curing property of the phenol-formaldehyde resins has been the greatest factor in bringing these products into commercial prominence. In the urea-formaldehyde series, resins are obtained which approach phenol-formaldehyde in rapidity of cure and which possess certain other highly desirable properties.

The observation that urea and formaldehyde would unite to form, on drying, a glass-like solid was heralded in years past as a discovery of prime importance. Considerable misapprehension arose to the effect that the clear material made in this way resembles glass in transparency, but is much tougher and more suitable for uses where the fragility of glass comes into question. Actually, urea resin "glass" is soft relative to glass itself, and is easily scratched. Also, because of inadequate water-resistance, the surface becomes dulled upon long exposure to humid conditions. Furthermore, the condensation processes continue to occur after the product has been made, and thus ultimately results in strains, cracks and disfigurements. Although the resins are insensitive to shock fracture, they can hardly be called "unbreakable." Thus, there are some limits to the excellence of the properties of the urea resins.

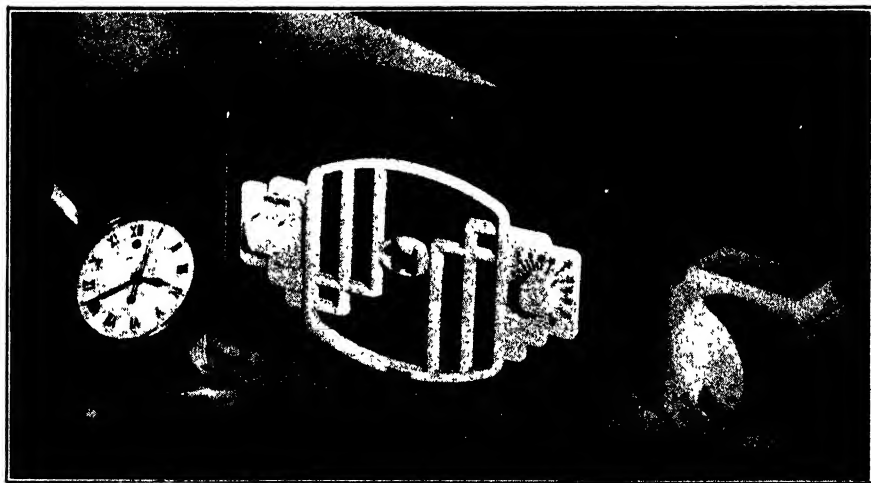
Fortunately, one of the undesirable properties of the urea resins, namely, their susceptibility to fissure formation, is minimized by the incorporation of substantial amounts of cellulose. A definite chemical affinity exists between the cellulose and the urea condensation product, and the resulting stock is permanent, translucent and strong.

An important advantage which the urea resin molding compositions possess over those of the phenol-formaldehyde type is the relative transparency of the molded goods, which makes possible a brilliancy and depth of color that is not easily obtained by any other thermosetting composition. Pigmentation of refined phenol-formaldehyde resins can result in very good shades, but articles molded from compositions so colored are decidedly opaque.

Not only are the exterior appearances or properties of the urea resins highly attractive, but the method of manufacture, and the nature of the raw materials required, is such as to make possible the production of these resins in enormous quantities. Urea is obtained by reaction between ammonia and carbon dioxide; consequently an almost unlimited supply could be obtained. Likewise, formaldehyde is made from methyl alcohol, and this in turn is a product of the hydrogenation of the oxides of carbon. It is a curious fact, and one which interests and puzzles the layman, that, by means of four gases, ammonia, carbon dioxide, carbon monoxide and hydrogen, it is possible to produce hard, solid materials. This

fact is brought home more emphatically because urea resins have been used to quite a large extent in the production of cups, saucers and other familiar utensils.

The steps by which the gaseous substances are ultimately converted into resins are such as to make possible the manufacture of various products of intermediate state of aggregation. Usually the reaction between urea and formaldehyde is carried out in aqueous solution, and the first result is the production of a hydrophilic colloid, which, on further condensation, becomes a hydrophobe. It is possible to check the condensation at the hydrophilic ("water-soluble") stage, and thus produce adhesives and impregnants. It is also possible to carry out the condensation of urea and formaldehyde in the presence of butyl alcohol, in which case the products are soluble in a wider variety of organic solvents, and consequently are more useful in the preparation of lacquers. ✓



*Courtesy Unyte Corporation*

FIG. 86.—A Portable Radio in a Two-Color Cabinet Molded of Unyte. Clock Cases of Unyte. The backs of the clock cases are molded solid with the sides, top and front.\*

\* Cabinet molded by Remler Co., Ltd.; clock cases by General Electric Co.

The hydrophobe is, of course, ordinarily used for making moldings. In this case, the process of thermosetting resembles that used in the manufacture of molded Bakelite, but there are a few essentials in which the two processes differ. Although a phenolic resin, on curing, undergoes chemical reactions which are substantially unalterable, the products of which probably are broken down only at ignition temperatures, the urea resin plastics, at a temperature between 130° and 140°C., form high-melting products, which, however, undergo a stage of decomposition, accompanied by softening, at a temperature of about 260°C. The property of hardening by chemical reaction at a temperature between 130° and 140° has been utilized in the plastics industry to a considerable extent, and, in the United States, there are several large concerns supplying molding compositions to the industry, the recognized brands being Unyte, Plaskon and Beetle (see Fig. 86).

The nature of the chemical reactions taking place during the condensations, and during the thermal hardening, is extremely complicated, and numerous con-

trols are required in order to establish the conditions necessary for the making of resin which can be converted into molded articles.

### THE MANUFACTURE OF UREA

No discussion of the production of urea would be complete without a mention of Wöhler's<sup>1</sup> classical preparation of this compound by the rearrangement of ammonium cyanate. Pure urea,  $\text{NH}_2\text{—CO—NH}_2$  (see Fig. 87), is a white crystalline substance, melting at  $132.6^\circ\text{C}.$ <sup>2</sup> and soluble in water, moderately soluble in alcohol and slightly soluble in benzene. The world's supply of this chemical is largely controlled by a German company.<sup>3</sup>

The increasing demand for urea of high-grade quality has led to the development of a number of synthetic processes for its technical preparation.<sup>4</sup> A commercial method of synthesis involves the use of by-product gases, carbon dioxide and ammonia.<sup>5</sup>

A mixture of carbon dioxide and ammonia is forced into an autoclave, forming ammonium carbamate,  $\text{NH}_4\text{CO}_2\text{NH}_2$ , which is maintained for 2 hours at the temperature ( $135^\circ\text{C}.$ ) required for its conversion to urea.<sup>6</sup> The reaction mass is then transferred to an apparatus in which it is distilled. A solution of urea is run off from the bottom and the unchanged ammonia and carbon dioxide are recovered at the top and returned to the compressor. To continue the process, more ammonia and carbon dioxide are supplied to the autoclave or an aqueous solution of ammonium carbamate or ammonium carbonate is added through the top of the apparatus. The urea solution is concentrated by vacuum evaporation or sprayed into a drying chamber, whence the product is obtained as a fine granular material. By saturating liquid ammonia with carbon dioxide, then heating to  $160\text{--}170^\circ\text{C}.$  under 75–80 atmospheres pressure, urea is formed in 40 per cent yield.<sup>7</sup> This yield is not improved by the use of catalysts, and corrosion during the process is considerable, necessitating the use of stainless steel (e.g., Krupp V4A) for the construction of the autoclave.<sup>8</sup> From a mixture of ammonia and carbon dioxide (molecular proportions, 2 to 1) at  $195^\circ\text{C}.$  and 230 atmospheres, a 47 per cent yield of urea was obtained in 30 minutes,<sup>9</sup> whereas using 10–15 per cent excess ammonia and heating at  $175\text{--}185^\circ\text{C}.$  at 150–175 atmospheres for 0.8–1.5 hours gave rise to a 50–60 per cent yield.<sup>10</sup>

Another process, utilizing synthetic ammonia made from gas mixtures of carbon dioxide, nitrogen and hydrogen is that of Hetherington and Krase.<sup>11</sup> The carbon dioxide is separated by absorption in a solution of an ammonium salt, and the nitrogen and hydrogen are combined to form ammonia, which is then reacted with the recovered carbon dioxide. Liquid ammonia and liquid carbon dioxide are delivered at

<sup>1</sup> F. Wöhler, *Pogg. Ann.*, 1828, 12, 253.

<sup>2</sup> Above its melting point urea dissociates into ammonia. B. H. Reeves (U. S. P. 1,982,539, Nov. 27, 1934, to Rockbestos Products Corp.; *Chem. Abs.*, 1935, 29, 527) treated an electrical conductor with a covering consisting of asbestos containing urea. On heating ammonia is evolved which serves as an arc-extinguishing agent.

<sup>3</sup> I. G. Farbenindustrie A.-G.

<sup>4</sup> For a review of urea production, see *British Plastics*, 1934, 5, 550.

<sup>5</sup> British P. 145,060, 1920, to Badische Anilin- & Soda-Fabrik; *Chem. Abs.*, 1920, 14, 3089. British P. 182,331, 1921; *Chem. Abs.*, 1922, 16, 4215. See also German P. 294,793, 295,075 and 295,389, 1914; *Chem. Abs.*, 1921, 15, 2101. From carbon monoxide and ammonia, formamide is obtained. P. L. Magill, *Ind. Eng. Chem.*, 1934, 26, 611.

<sup>6</sup> See also L. Casale, Canadian P. 259,273, 1926, and British P. 241,123, 1924; *Chem. Abs.*, 1926, 20, 2333. H. W. De Ropp and H. C. Hetherington, Canadian P. 342,938, 1934, to Canadian Industries, Ltd.; *Chem. Abs.*, 1934, 28, 7263. M. Tokusaka, *J. Agr. Chem. Soc. Japan*, 1934, 10, 1333; 1935, 11, 107; *Chem. Abs.*, 1935, 29, 2919, 4334.

<sup>7</sup> G. A. Yakovlev, *J. Applied Chem. (Russia)*, 1928, 1, 70; *Chem. Abs.*, 1929, 23, 1880.

<sup>8</sup> In urea synthesis involving the heating of ammonia and carbon dioxide in a chrome steel vessel, the metal surfaces exposed to the vapors above the reaction mixture can be protected by treatment with a copper ammonium carbonate solution. (H. C. Hetherington and H. W. De Ropp, U. S. P. 1,986,973, Jan. 8, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 1382.)

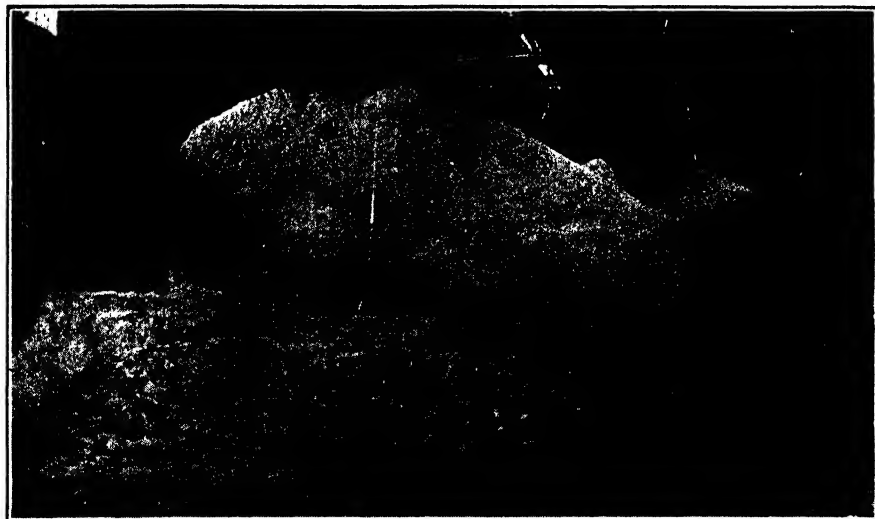
<sup>9</sup> B. A. Bolotov and A. N. Popova, *J. Chem. Ind. Russ.*, 1934, 10 (9), 32; *Brit. Chem. Abs. B*, 1935, 12. B. I. Levi (*J. Chem. Ind. (Moscow)*, 1934, 9, 38; *Chem. Abs.*, 1935, 29, 457) has discussed the best conditions for the synthesis of urea from carbon dioxide and ammonia.

<sup>10</sup> B. A. Bolotov and A. N. Popova, *J. Chem. Ind. (Moscow)*, 1934, 9, 32; *Chem. Abs.*, 1935, 29, 457.

<sup>11</sup> H. C. Hetherington and H. J. Krase, U. S. P. 1,780,208, Oct. 1, 1929, to A. B. Lamb; *Chem. Abs.*, 1929, 23, 5476.

controlled rates into a lead-lined jacketed autoclave, which is heated to  $150^{\circ}\text{C}.$ , the pressure rising to 100-110 atmospheres.<sup>12</sup> A maximum conversion of 35-50 per cent is attained, after which unchanged ammonium carbamate is decomposed to recover its component gases, urea solution being discharged from the still (see Figs. 88 and 89). The gaseous mixture on which the process operates is obtained by the catalytic oxidation with steam of a semi-water gas produced by the action of air and steam on hot coke.<sup>13</sup> Ammonium nitrate or chloride is used as the absorbent for carbon dioxide.

Pure urea may be obtained from the technical product by the treatment of concentrated, slightly ammoniacal solutions with oxidizing agents,<sup>14</sup> e.g., air, oxygen or manganese dioxide. Heavy metals are thereby precipitated, and pure colorless urea can be crystallized from the solution. Alternatively, the concentrated solu-



Courtesy I. G. Farbenind. A.-G.

FIG. 87.—50,000,000 Pounds of Urea.

tion containing about 70 per cent of urea and 1.5 per cent of ammonia obtained directly from the synthesis is treated with a fine spray of air at  $70-75^{\circ}\text{C}.$  to give the pure compound.<sup>15</sup>

A further modification of the urea synthesis consists in heating a dry liquefied mixture of carbon dioxide and ammonia to  $80-120^{\circ}\text{C}.$ <sup>16</sup> Carbon dioxide may be replaced by carbon oxysulphide, forming ammonium thiocarbamate which may be converted into urea.<sup>17</sup> For example, 5 parts of ammonia are liquefied in a steel autoclave, and 2.6 parts of carbon oxysulphide introduced. The mixture is heated to  $120^{\circ}\text{C}.$  for 2 hours, at which time the pressure, created by the hydrogen sulphide formed in the reaction, reaches about 18 atmospheres. The contents are extracted with water, and filtered from any impurities (usually iron sulphide from the walls of the container) giving a 70-80 per cent yield of urea. Urea can be prepared in

<sup>12</sup> H. J. Krase, V. L. Gaddy and K. G. Clark, *Ind. Eng. Chem.*, 1930, 22, 289. K. G. Clark, V. L. Gaddy and C. E. Rist, *ibid.*, 1933, 25, 1092.

<sup>13</sup> A. B. Lamb, British P. 335,913, 1929; *Brit. Chem. Abs.* B, 1931, 12.

<sup>14</sup> British P. 249,041, 1925, to Badische Anilin- & Soda-Fabr.; *Brit. Chem. Abs.* B, 1926, 420.

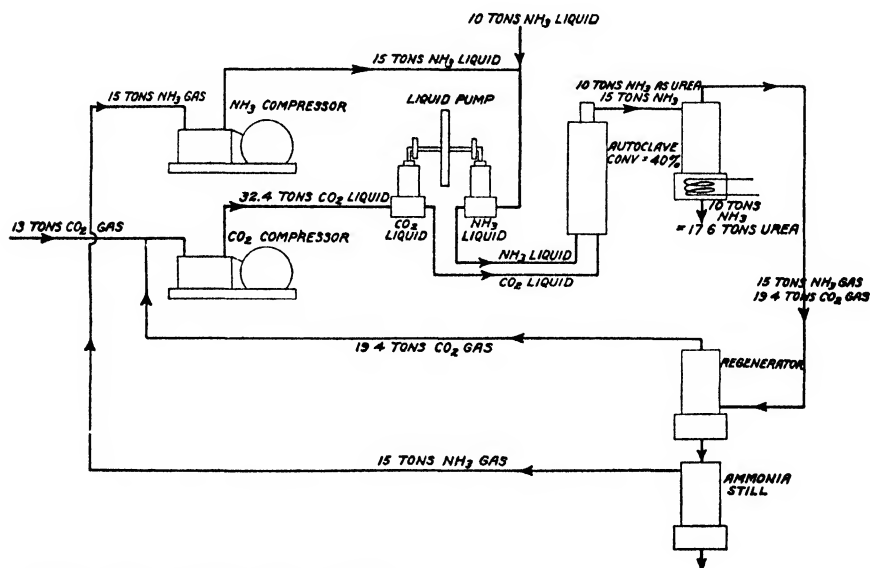
<sup>15</sup> L. Bub, U. S. P. 1,659,190, Feb. 14, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 1365.

<sup>16</sup> French P. 675,439, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2761.

<sup>17</sup> A. Klemenc and R. Schoeller, U. S. P. 1,808,465, June 2, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4287. See also British P. 327,026, 1929; *Chem. Abs.*, 1930, 24, 4793.

96 per cent yield by the oxidation of uric acid with chromic-sulphuric acid mixture.<sup>18</sup>

According to Hofsäsz,<sup>19</sup> improved thermal economy and convenience of working in the conversion of ammonium carbamate to urea are attained by compressing carbon dioxide and ammonia with a viscous oil to form a paste containing up to 50 per cent of ammonium carbamate. This is pumped into a chamber at 150-200°C., the pressure being 100 atmospheres, where 40 per cent conversion to urea occurs. Removal of carbon dioxide and ammonia by distillation leaves a solution



Courtesy Industrial and Engineering Chemistry

FIG. 88.—Flow Diagram for a Direct Synthetic Urea Process. (H. J. Krase, V. L. Gaddy and K. G. Clark.)

of urea and a layer of oil which is returned to the autoclave. Barsky and Griffith<sup>20</sup> obtained urea from cyanamide by adjusting the acidity of the cyanamide solution to 0.1 N and heating at 60°C. Substantially all of the cyanamide is converted to urea under these conditions.

### THE CHEMISTRY OF THE UREA SYSTEM

Empirical observation played an important part in the early development of urea resins. The chemistry of the processes involved had not been worked out, and it is only as a result of more recent work that much information concerning the course of the various reactions occurring, and the structures of the polymerized products, has been obtained. The condensation is conditioned by a certain

<sup>18</sup> J. Schwander and H. Cordebard, *Bull. soc. chim. biol.*, 1928, 10, 920; *Brit. Chem. Abs. A*, 1928, 1283.

<sup>19</sup> M. Hofsäsz, U. S. P. 1,945,314, Jan. 30, 1934, to N.-V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, 28, 2372.

<sup>20</sup> G. Barsky and P. W. Griffith, U. S. P. 1,758,641, May 13, 1930, to American Cyanamid Co.; *Chem. Abs.*, 1930, 24, 3251.



tautomeric mobility of the carbamide system, and the detailed consideration of the condensation process and the structure of the resins may accordingly be prefaced by a review of recent work on the chemistry of urea and its related compounds, which sheds some light on the condensations involved in resin formation.

Davis<sup>21</sup> considered the various possible modes of fission by which urea, or urea derivatives, might break down, and the various modes of recombination. The large

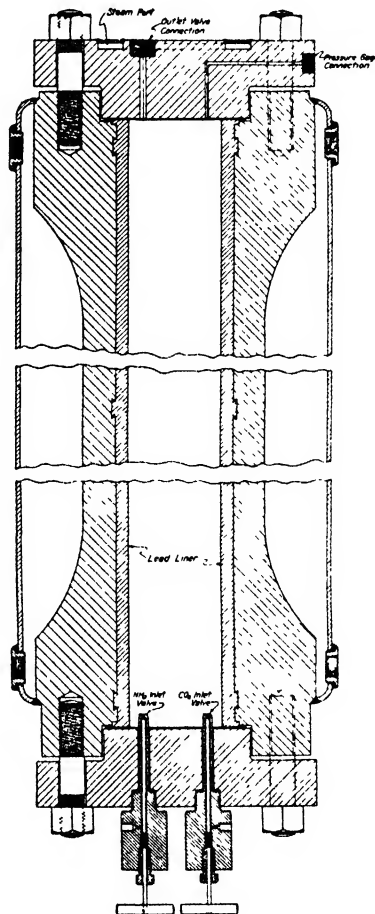
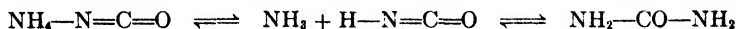


FIG. 89.

Autoclave Used in the Synthesis of Urea from Liquid Ammonia and Liquid Carbon Dioxide. A small naval gun formed the basis of the apparatus. (H. J. Krase, V. L. Gaddy and K. G. Clark.)

*Courtesy Industrial and Engineering Chemistry*

number of possibilities in the case of simple molecules portends great complications when highly condensed molecules of urea resin are to be considered. Ammonia and cyanic (or isocyanic) acid enter into reversible combination in two ways



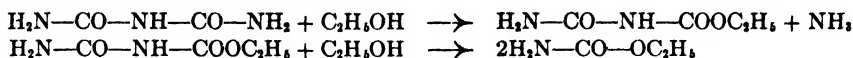
Blair<sup>22</sup> has suggested that in aqueous solution hydrated forms of urea may exist, and accordingly the dearrangement may be formulated as follows:

<sup>21</sup> T. L. Davis, *Proc. Nat. Acad. Sci.*, 1925, 11, 68.

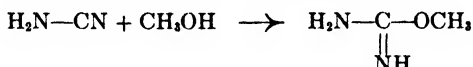
<sup>22</sup> J. S. Blair, *J.A.C.S.*, 1926, 48, 87.



The representation of the preceding compounds as ammonocarbonic acids is supported by the preparation of such salts as potassium-urea ( $K_2H_5CON_3$ ) in liquid ammonia solution.<sup>56</sup> The action of water is usually to effect complete hydrolysis to carbamate or carbonate, but by the use of anhydrous ethyl alcohol, various intermediate stages have been isolated.<sup>57</sup> Thus biuret is progressively alcoholized to ethyl allophanate and urethan:

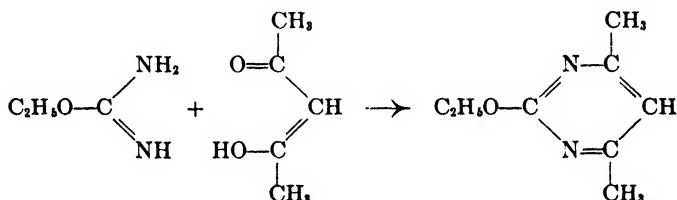


By the addition of alcohol to the nitrile group of cyanamide, derivatives of the isoureas are formed<sup>58</sup> as indicated in the following equation:

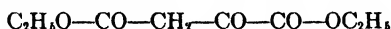


However, the n-propyl and n-butyl isoureas, obtained in a similar manner, form semi-solid uncrystallizable masses.

Substituted isoureas react with diketones and ketonic esters,<sup>59</sup> and in some cases cyclic products are formed, as in the condensation of ethyl isocarbamide and acetylacetone:

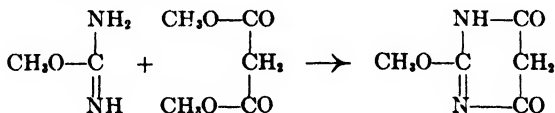


Ethyl acetopyruvate ( $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CO}-\text{CO}-\text{OC}_2\text{H}_5$ ) undergoes vigorous condensation to yield, however, an ill-defined gummy product. This tendency is also encountered with ethyl oxaloacetate



In the latter case there is evidence that the presence of impurities favors the formation of amorphous, probably high molecular, products.

The manner in which stable cyclic structures tend to be formed from the mobile urea system is shown by the condensation of isoureas with malonic ester, whereby barbituric acid derivatives are formed.<sup>60</sup>



Reactions essentially similar to those of urea take place with guanidine. Dicyanodiamide can dearrange in two senses,<sup>61</sup> and when heated above its melting point yields the products, ammonia, cyanamide, melamine and melon, the latter two compounds being trimers of cyanamide and dicyanimide, respectively.

<sup>56</sup> J. S. Blair, *J.A.C.S.*, 1926, 48, 97.

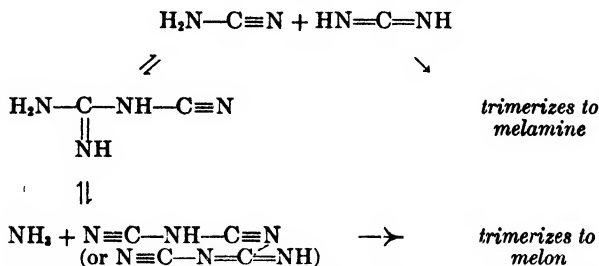
<sup>57</sup> J. S. Blair, *J.A.C.S.*, 1927, 49, 509.

<sup>58</sup> S. Basterfield and M. S. Whelan, *ibid.*, 1927, 49, 3177.

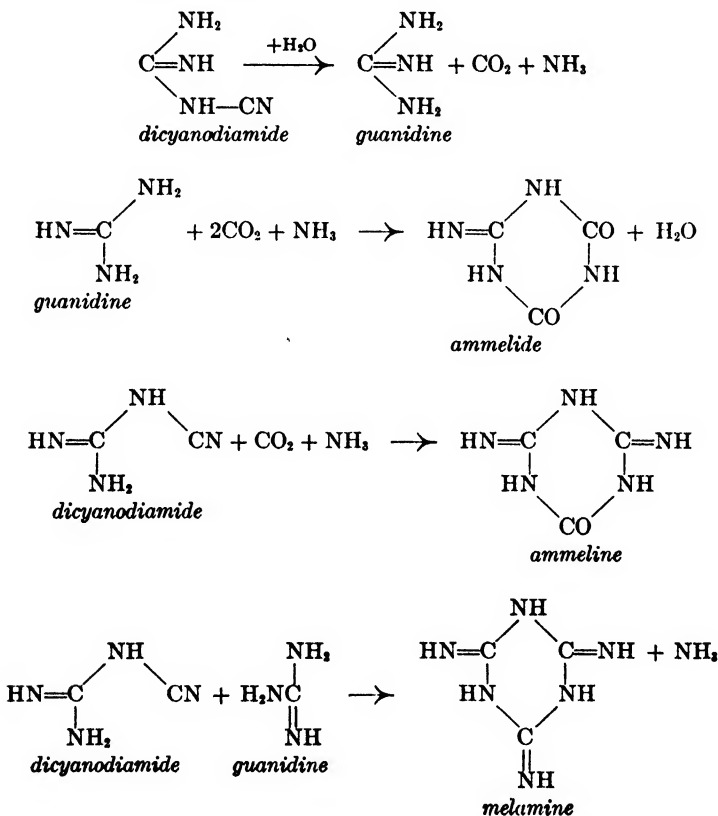
<sup>59</sup> S. Basterfield and E. C. Powell, *Can. J. Research*, 1929, 1, 285; *Chem. Abs.*, 1930, 24, 618.

<sup>60</sup> S. Basterfield and E. C. Powell, *Can. J. Research*, 1929, 1, 281; *Chem. Abs.*, 1930, 24, 1356.

<sup>61</sup> T. L. Davis, *loc. cit.*



Melamine and melon contain six-membered rings of alternating carbon and nitrogen atoms. The tendency for such rings to form is illustrated<sup>23</sup> by the following reactions in the guanidine series:



Substituted (aryl) guanidines may be prepared<sup>24</sup> by the action of amines upon methyl isothiurea sulphate, and dicyanodiamide may be condensed with o-amino phenol<sup>25</sup> to yield a benzoxazole guanidine derivative. The substituted guanidines and ureas undergo rearrangements paralleling those of the parent compounds,<sup>26</sup> and the fission products polymerize in a corresponding manner. Thus, if in the

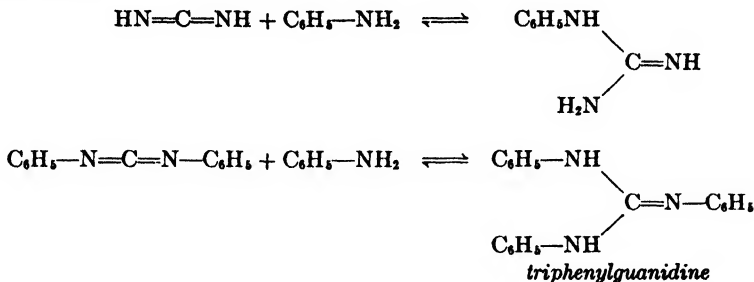
<sup>23</sup> G. B. L. Smith, V. J. Sabetta and O. F. Steinbach, Jr., *Ind. Eng. Chem.*, 1931, 23, 1124.

<sup>24</sup> G. B. L. Smith, *J.A.C.S.*, 1929, 51, 476.

<sup>25</sup> G. B. L. Smith, J. H. Kane and C. W. Mason, *J.A.C.S.*, 1929, 51, 2522.

<sup>26</sup> T. L. Davis and K. C. Blanchard, *J.A.C.S.*, 1929, 51, 1790.

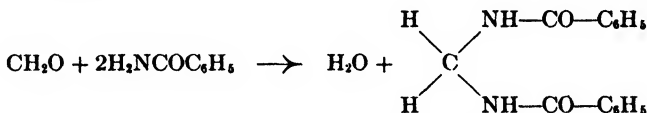
dearrangement scheme we replace carbodiimide,  $\text{HN}=\text{C}=\text{NH}$ , by diphenylcarbodiimide,  $\text{C}_6\text{H}_5-\text{N}=\text{C}=\text{N}-\text{C}_6\text{H}_5$ , the crystalline trimer<sup>36</sup> of that substance takes the place occupied by melamine. Instead of combining with itself to form a trimer, diphenylcarbodiimide may unite with a mol of aniline in a manner which also sustains the parallelism,



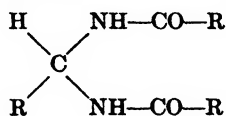
It is of interest to note that triphenylguanidine, when heated for two hours at  $180^\circ\text{C}$ ., is converted into an amber-colored, brittle, glassy resin. The transformations in the thiourea series are similar to those encountered in the case of urea or guanidine.<sup>37</sup>

#### CONDENSATION OF ALDEHYDES AND KETONES WITH UREA

Amides in general undergo condensation with formaldehyde. In 1892, Pulvermacher<sup>38</sup> observed that in acid solution formaldehyde reacted with benzamide according to the equation,



Einhorn<sup>39</sup> isolated a different crystalline product,  $\text{C}_6\text{H}_5\text{CONHCH}_2\text{OH}$ , which he obtained both in acid and in alkaline solution. With formamide or acetamide, formaldehyde gave colorless syrupy products. The methylol-amide type of structure has since attained great importance in the chemistry of the urea resins. Recent studies<sup>40</sup> have shown that the Pulvermacher structure



is also often formed.

Weber and Tollens<sup>41</sup> observed that uric acid forms a number of "addition compounds" with formaldehyde. Sachs<sup>42</sup> pointed out an analogy between these addition compounds and the product obtained from phthalimide,

<sup>36</sup> W. Weith, *Ber.*, 1874, 7, 10, 1305. A. Laubenheimer, *ibid.*, 1880, 13, 2155. C. Schall and S. Paschkowsky, *ibid.*, 1892, 25, 2880. C. Schall, *ibid.*, 1893, 26, 3064; 1894, 27, 2260. H. N. McCoy, *ibid.*, 1897, 30, 1090.

<sup>37</sup> K. H. Stotta and H. Dressler, *Ber.*, 1920, 63, 888.

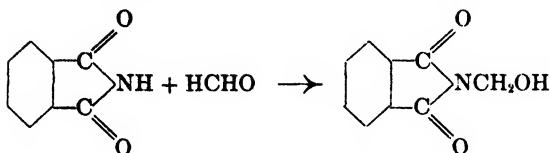
<sup>38</sup> G. Pulvermacher, *Ber.*, 1892, 25, 304.

<sup>39</sup> A. Einhorn, German P. 157,355, 1902 and 158,088, 1902. See also German P. 164,610 and 164,611, 1902, to Kalle & Co.; *Chem. Zentr.*, 1905, 2, 1751.

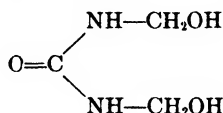
<sup>40</sup> W. A. Noyes and D. B. Forman, *J.A.C.S.*, 1933, 55, 3493.

<sup>41</sup> K. Weber and B. Tollens, *Ann.*, 1898, 299, 340.

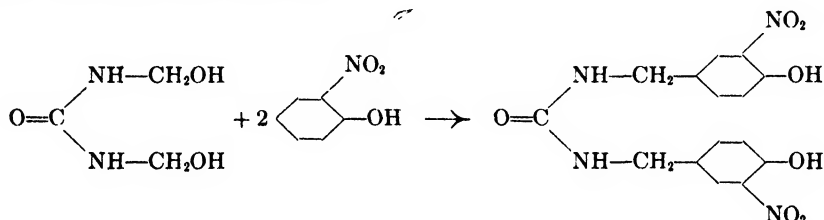
<sup>42</sup> F. Sachs, *Ber.*, 1898, 31, 3280.



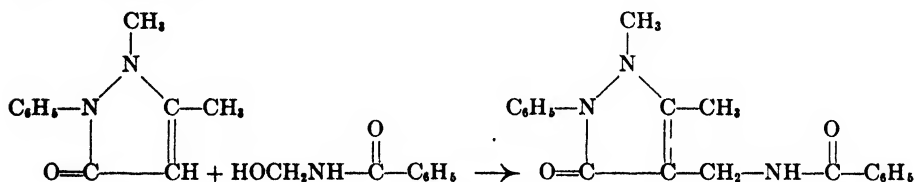
Postponing, for the moment, a more detailed discussion of the reaction between urea and formaldehyde, suffice it to say at this point that an important intermediate in the reaction between these two substances is dimethylolurea.



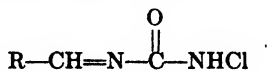
In acid solution, dimethylolurea reacts with benzene derivatives, such as o-nitrophenol, according to the equation:<sup>48</sup>



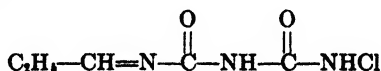
The related compound methylolbenzamide has been found by Monti<sup>49</sup> to undergo condensation with such representative  $\beta$ -diketones as benzoylacetone. With antipyrine, a condensation takes place in concentrated sulphuric acid to yield a resinous precipitate from which 4-benzoylaminomethyl-1,5-dimethyl-2-phenyl pyrazolone was isolated.



Although urea readily forms methylolurea derivatives with formaldehyde, monochlorourea ( $\text{NH}_2\text{—CO—NHCl}$ ), according to Ottensooser,<sup>48</sup> reacts with aldehydes to form compounds of a different type such as



Two urea residues may be involved in the condensation. For example, the product from propionaldehyde is:



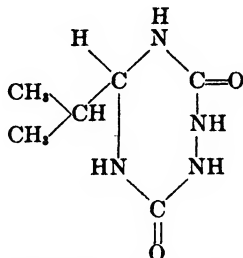
The corresponding compound from isobutylchlorourea was not the final product

<sup>48</sup> H. de Diesbach, O. Wanger and A. von Stockalper, *Helv. Chim. Acta*, 1931, 14, 355; *Brit. Chem. Abs. A*, 1931, 614.

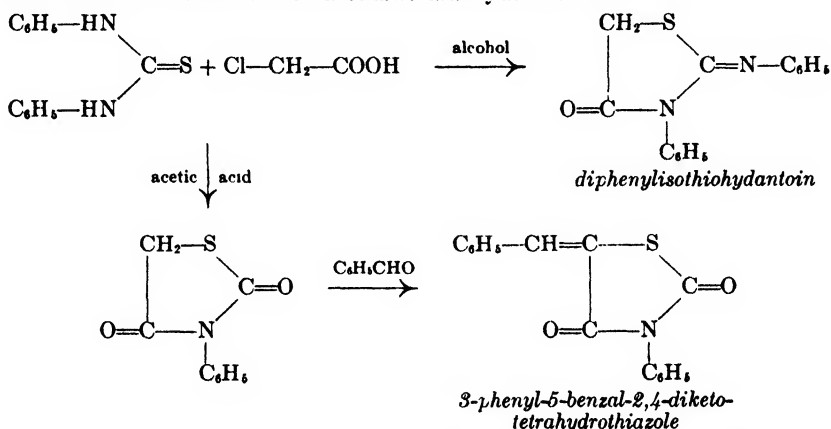
<sup>49</sup> L. Monti, *Gazz. chim. ital.*, 1930, 60, 39; *Chem. Abs.*, 1930, 24, 4013.

<sup>48</sup> M. R. Ottensooser, *Bull. soc. chim.*, 1929, (4) 45, 1013; *Chem. Abs.*, 1930, 24, 3755.

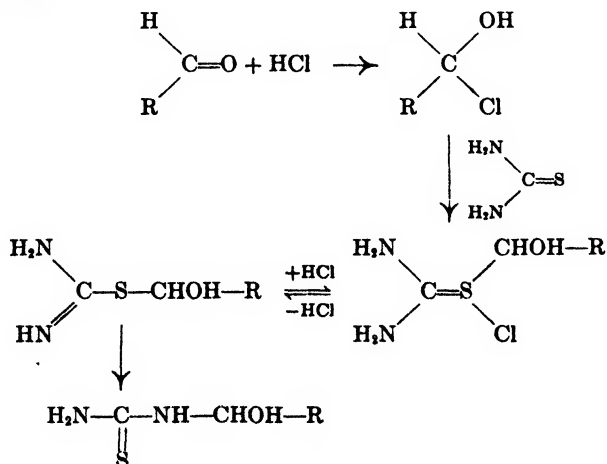
when 5 per cent potassium hydroxide was used as a condensing agent, for ring closure occurred forming



Thiocarbanilide reacts with chloroacetic acid to give isothiohydantoin or diketo-tetrahydrothiazoles depending upon the type of solvent used.<sup>46</sup> The latter compound enters into reaction with aromatic aldehydes as indicated.



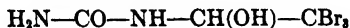
Taylor<sup>47</sup> found that ketones and aromatic aldehydes condensed with thiourea in the presence of hydrogen chloride giving sulphur-substituted derivatives, which underwent rearrangement on removal of the acid, forming compounds related to the methylolureas:



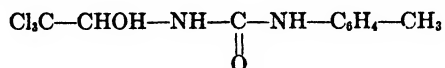
<sup>46</sup> K. S. Markley and E. E. Reid, *J.A.C.S.*, 1930, 52, 2137.

<sup>47</sup> J. Taylor, *J.C.S.*, 1922, 121, 2267.

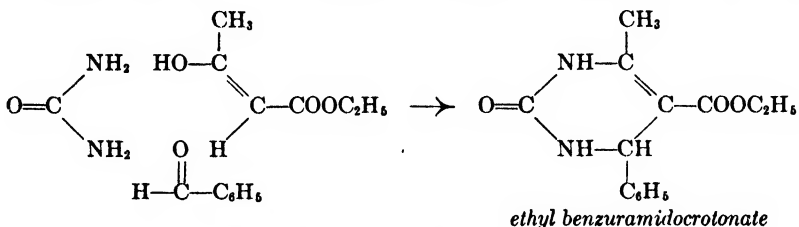
Bromal hydrate condenses with urea forming bromalurea, from which ethers may be obtained.<sup>48</sup> This behavior indicates that the bromalurea possesses the following structure:



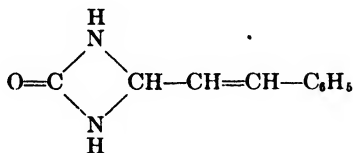
Dibromalureas are formed in an analogous manner. Chloral hydrate<sup>49</sup> reacts similarly with tolyl- and nitrophenylureas, giving compounds of the type



Simultaneous condensation of urea with benzaldehyde and ethyl acetoacetate gives ethyl benzuramidocrotonate.<sup>50</sup> Resinous substances were obtained from benzur-



amidocrotonic ester by Biginelli<sup>51</sup> who isolated from the products of sodium-amalgam reduction a glassy solid (m. p. 59-60°C.), which he assumed to be a mixture of two isomeric benzuramidobutyric esters. Condensation of m-nitrobenzaldehyde and acetoacetic ester in equimolecular proportions with urea resulted in the production of an insoluble solid, and a substance deposited from hot alcohol as a jelly-like mass. From urea and cinnamic aldehyde, a cinnamic ureide of reddish color was obtained, resembling porcelain in appearance, to which the following structure was assigned:



#### CHEMISTRY OF THE UREA-FORMALDEHYDE REACTION

The foregoing brief survey of the chemistry of urea may serve to bring out certain points of importance in the interpretation of the structure of the urea-formaldehyde resins and the mechanism of the resinification process. Attention may be drawn especially to the tendency to form methylolureas; the mobility of the carbamide system which enables reaction to proceed from either the urea or the isourea structure; the ease of polymerization, either with or without the elimination of water and ammonia; and finally, the readiness with which cyclic structures are formed in the polymerization process.

The reaction of formaldehyde with urea was early studied by Goldschmidt,<sup>52</sup>

<sup>48</sup> F. D. Chattaway and E. J. F. James, *Proc. Roy. Soc.*, 1932, A137, 481; *Chem. Abs.*, 1932, 26, 5549.

<sup>49</sup> F. D. Chattaway, G. M. T. Kerr and C. G. Lawrence, *J.C.S.*, 1933, 30.

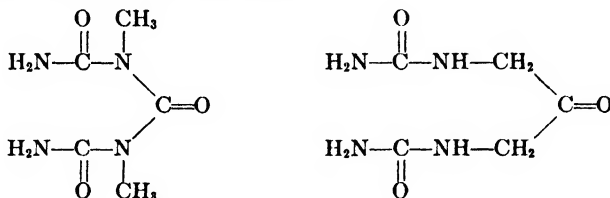
<sup>50</sup> L. H. Hinkel and D. H. Frey, *Rec. trav. chim.*, 1929, 48, 1280; *Chem. Abs.*, 1930, 24, 853.

<sup>51</sup> P. Biginelli, *Gazz. chim. Ital.*, 1893, 23, 366; *J.C.S.*, 1893, 64, 645.

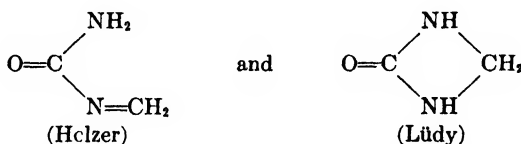
<sup>52</sup> C. Goldschmidt, *Ber.*, 1896, 29, 2438.



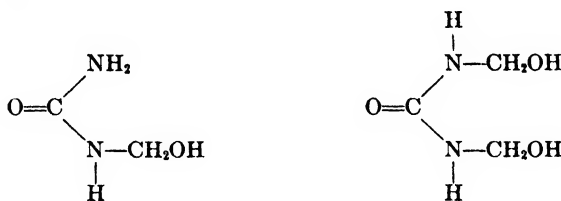
who by effecting condensation in neutral, or better in acid, solution obtained a white granular substance which, according to analysis, may be represented by the formula  $C_5H_{10}N_4O_5$ . If the reaction is considered as taking place between 2 mols of urea and 3 of formaldehyde with the elimination of 2 mols of water, then, the resulting compound might possess structures such as



The later work of Dixon<sup>53</sup> indicated that these structures were erroneous. A different substance had already been obtained by Hölzer<sup>54</sup> and Lüdy<sup>55</sup> in the form of methyleneurea,  $C_2H_4N_2O$ . This compound was formulated in two different ways, namely:



Another simple compound which was early isolated<sup>56</sup> from reaction products of urea and formaldehyde in alkaline solution is dimethylolurea. It was noted that this substance gave off formaldehyde on boiling with water or mineral acids. Two crystalline compounds were later prepared by Einhorn<sup>57</sup> who used barium hydroxide as a condensing agent. Investigation showed that these compounds were mono- and dimethylolurea



Methylolurea compounds were first thoroughly investigated by Einhorn and Hamburger.<sup>58</sup> They showed that the composition of the products obtained varied considerably with the conditions of condensation, but that the methylolureas were indeed the first condensation products, and could be isolated if the alkaline condensing agent were neutralized before further reaction occurred. Using barium hydroxide as condensing agent, and neutralizing with carbon dioxide, dimethylolurea,  $\text{CO}(\text{NH}-\text{CH}_2\text{OH})_2$ , was isolated as a crystalline, easily soluble body melting about  $126^\circ\text{C}$ ., but changing at  $137^\circ\text{C}$ . to an amorphous substance decomposing at  $260^\circ\text{C}$ . An insoluble amorphous precipitate was deposited from dimethylolurea solutions by the action of alkalis and to a lesser extent by acids, but no well-defined sub-

<sup>53</sup> A. E. Dixon, *J.C.S.*, 1918, 113, 238.

<sup>54</sup> Hölzer, *Ber.*, 1884, 17, 659; 1885, 18, 3302. B. Tollens, *Ber.*, 1896, 29, 2751.

<sup>55</sup> E. Lüdy, *Monatshefte*, 1889, 10, 295; *J.C.S.*, 1889, 56, 1059.

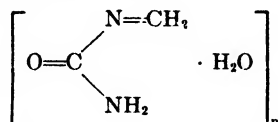
<sup>56</sup> C. Goldschmidt, *Chem. Ztg.*, 1897, 46, 480; *J.C.S.*, 1898, 74 (1), 178.

<sup>57</sup> A. Einhorn, *Ann.*, 1908, 361, 113; *Chem. Abs.*, 1908, 2, 2682.

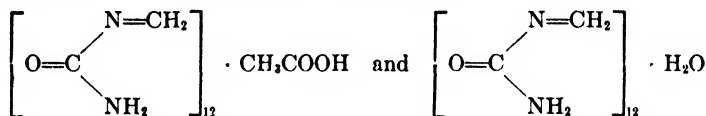
<sup>58</sup> A. Einhorn and A. Hamburger, *Ber.*, 1908, 41, 24.

stance of constant composition was observed. Monomethylolurea,  $\text{NH}_2\text{—CO—NH—CH}_2\text{OH}$ , was obtained by using a small proportion of barium hydroxide as condensing agent, and neutralizing with carbon dioxide immediately. The addition of dilute acids produced immediate deposition of a flocculent amorphous precipitate which, as with the previous product, yielded no definite chemical entity.

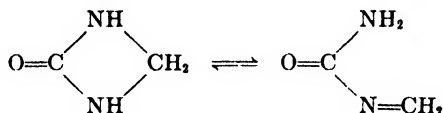
Scheibler, Trostler and Scholz<sup>80</sup> have investigated the further stages of the condensation, with the result that the preliminary formation of monomethylolurea, when neutral formaldehyde was used, has been confirmed. This when pure, was found to be transformed by a trace of hydrochloric acid into a high-molecular-weight product of the same composition. However the polymer is not considered as consisting of methylolurea units, but rather units of methyleneurea each containing one firmly bound molecule of water:



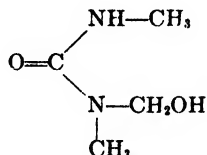
On the other hand when methylolurea is treated with glacial acetic acid, two well characterized modifications of methyleneurea were obtained. Of the two compounds so produced, one is soluble in glacial acetic acid and contains one mol of acetic acid in combination with an average of 12 mols of methyleneurea, whereas the other contains 1 mol of water in combination with the same number of methyleneurea units and is insoluble in acetic acid.



According to van Laer,<sup>81</sup> the two forms of methyleneurea (vide supra) are in tautomeric equilibrium:



However, when symmetrical dimethylurea was condensed with formaldehyde, a monomethylol derivative was obtained.

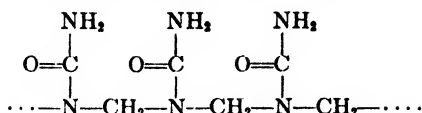


No cyclization or polymerization occurs in this case, a fact which could be interpreted as indicating that the ( $\text{N=CH}_2$ ) group is the one which is involved in the polymerization of methyleneurea. Furthermore, the polymerization of methyleneurea may then be readily conceived as a process analogous to that which takes place in the formation of polyoxymethylene<sup>81</sup> long-chain molecules: e.g.,

<sup>80</sup> H. Scheibler, F. Trostler and E. Scholz, *Z. angew. Chem.*, 1928, 41, 1305; *Chem. Abs.*, 1929, 23, 2425.

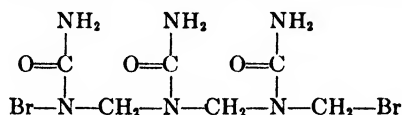
<sup>81</sup> M. van Laer, *Bull. soc. chim. Belg.*, 1919, 28, 381; *Chem. Abs.*, 1922, 16, 2113.

<sup>82</sup> H. Staudinger, *Ber.*, 1926, 59, 3019.

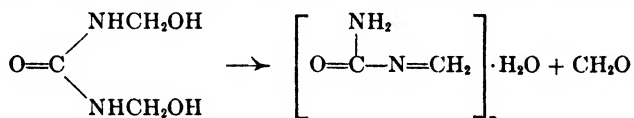


From this formula it may be seen how a molecule of acetic acid or a molecule of water might add on to the free valencies at the end of the chains, forming the acetic-acid-soluble and insoluble compounds already mentioned.

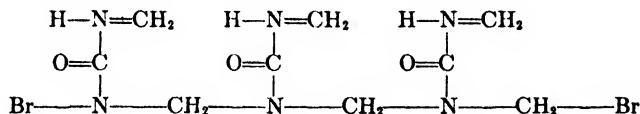
In a similar manner, halogens may add on to the polymethyleneurea chains. Such substances, formed in glacial acetic acid solutions, according to Scheibler, Trostler and Scholz,<sup>22</sup> are not very stable, but give up their halogen on standing in the air, or on slight warming. The *loose* bromine compound formed in this way contains too little bromine to be a bromamine or bromamide, but corresponds to the bromine addition compound of a trimeric methyleneurea:



Starting with two mols of formaldehyde to one mol of urea, the known dimethylolurea constitutes the initial product, but readily splits off formaldehyde on standing, with formation of the polymerized methyleneurea previously described:



Insoluble compounds are not obtained when dimethylolurea is dissolved in cold acetic acid, but upon addition of an acetic acid solution of bromine, a bromine addition product precipitates. Analysis for bromine indicates that this compound contains 3 dimethyleneurea residues.



A trimeric crystalline methylolmethylenurea, combined with one molecule of water, is produced by condensation of two molecules of formaldehyde with one mol of urea in the presence of a little ammonia, and corresponds exactly with the bromide described. In contradistinction to the well-defined compounds here discussed, the use of caustic alkalis as condensing agents has been found to lead to products of variable composition.

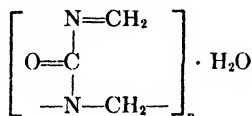
In addition to following the successive steps of the condensation process, Scheibler and co-workers studied the degradation of the synthetic resinous mass. By prolonged boiling with glacial acetic acid, the substance is dissolved completely, and addition of absolute alcohol then precipitates a white amorphous substance which is soluble in cold water. Formaldehyde and methylamine are evolved in the solution step, the latter being found only in the presence of a little water. The origin of methylamine may be attributed to the separation of a  $(-\text{N}-\text{CH}_2-)$  group by hydrolytic fission, which is then reduced by formaldehyde. The degrada-

<sup>22</sup> H. Scheibler, F. Trostler and E. Scholz, *loc. cit.*

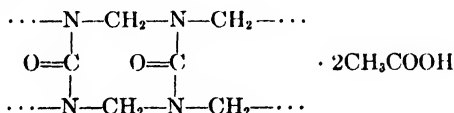
tion product may be acetylated with acetic anhydride to give acetyl derivatives which, in turn, yield bromine addition compounds resembling those obtained synthetically and described above. Therefore, degradation evidently yields a polymeric methylene- or methylolmethyleurea.

The conception of the polymerized mass afforded by the study of the degradation is that of chains of dimethyleneurea or methylolmethyleurea units joined together, the free ends of the chains being attached to water molecules. Such chains may be associated by secondary valence forces into micelles and colloid particles, conferring on the polymerized material its characteristically high-molecular physical properties. Degradation leads to replacement of the terminal water molecules by acetic acid, or bromine, with possibly a simultaneous shortening of the mean chain length.

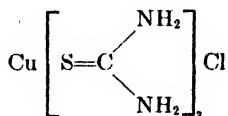
It is to be noted that the polydimethyleneurea products cannot be hydrogenated, and so do not in reality contain the azomethane grouping implied by the formulation



It is believed, therefore, that saturation is possibly achieved by a process of ring formation, according to the general scheme:

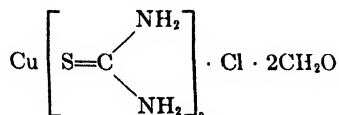


Walter and Oesterreich<sup>28</sup> have applied an interesting method to the study of the condensation process, by utilizing the ability of thiocarbamide to enter into complex compound formation with metal salts. Thus, with cuprous chloride, thiourea forms the stable complex

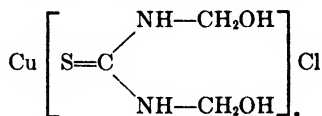


The complex salt, in turn, undergoes reaction with formaldehyde to yield colloidal solutions from which flocculent precipitates may be obtained upon addition of potassium chloride. These precipitates differ from those obtained in the urea-formaldehyde condensation, in that they may readily be dried for analysis. Such complex salts offer the additional advantage that the copper and chlorine content permit of less ambiguous analysis than is possible with dried urea-formaldehyde products. This last-named fact, coupled with cryoscopic measurements, enables some evidence to be obtained as to the complexity of the condensed system. Yellow viscous solutions with identical properties were obtained first by the action of formaldehyde (6 mols) on the cuprous chloride complex mentioned above; secondly, by the simultaneous reaction of equivalent amounts of thiourea, formaldehyde and cuprous chloride; and thirdly by the action of dimethylolthiourea on cuprous chloride. Evaporation of the solution obtained by the first method afforded a resin of the approximate composition

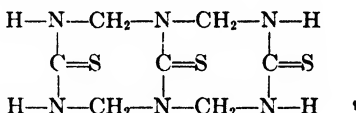
<sup>28</sup> G. Walter and K. Oesterreich, *Kolloid-Beihfte*, 1931, 34, 115; *Chem. Abs.*, 1932, 26, 3682. G. Walter and H. Lutwak, *Kolloid-Beihfte*, 1934, 40, 158; *Chem. Abs.*, 1935, 29, 5198.



The second reaction, involving the action of both methylol- and dimethylolthiourea on cuprous chloride, yielded a substance approximating



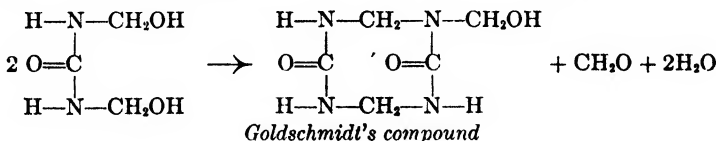
which upon polymerization by heat, gives a product of lower copper content. The identity of the products from the mono- and dimethylolureas is attributed to the initial formation of dicyclic structures:



Such structures are, then, coordinatively linked to the copper through the secondary nitrogen atoms. The cryoscopic investigation of solutions of dimethylolurea, with and without addition of cuprous chloride, indicated that mild polymerization led only to an increase in the proportion of dicyclic polymers as compared with straight-chain polymers. Prolonged heating led to loss of formaldehyde and water, and Walter considered that the resins formed were probably represented by a tetracyclic structure.

The conclusion drawn by Walter<sup>64</sup> from the evidence of this work is that a relatively low molecular weight must be assigned to the urea-formaldehyde resins, the resinous properties being attributable, presumably, to colloidal association.

According to Dixon,<sup>65</sup> dimethylolurea loses water and formaldehyde, when heated above its melting point, to yield a compound which appears to be identical with Goldschmidt's product, discussed earlier in this section.<sup>66</sup>



By using a trace of sodium acetate as a condensing agent and neutralizing as soon as fusion occurs, typical glassy resinous end products were obtained.

Evidence for the formation of ramified chains and cyclic structures in the urea-formaldehyde condensation has been obtained by Walter and Gewing<sup>67</sup> from the analytical study of the water and formaldehyde lost during the process. If the molar ratio

$$\frac{\text{water lost}}{\text{urea in substance}}$$

<sup>64</sup> G. Walter, *Kolloid-Z.*, 1931, 57, 229; *Chem. Abs.*, 1932, 26, 4486. See also R. Houwink, *British Plastics Year Book*, 1935, 51.

<sup>65</sup> A. E. Dixon, *J.C.S.*, 1918, 113, 238.

<sup>66</sup> C. Goldschmidt, *Ber.*, 1896, 29, 2438.

<sup>67</sup> G. Walter and M. Gewing, *Kolloid-Beihfte*, 1931, 34, 163; *Chem. Abs.*, 1933, 26, 3941.

be denoted by  $W$ , and the molar ratio

$$\frac{\text{formaldehyde lost}}{\text{urea in substance}}$$

by  $F$ , it can readily be seen from previous considerations that the condensation of dimethylolurea units to form Goldschmidt's compound would yield the following values:

$$\begin{aligned} W &= 1 \\ F &= 0.5 \end{aligned}$$

Actually, Walter and Gewing found that dimethylolurea condensed with itself in the absence of catalysts in such a way as to give 1.007 mols of water and 0.4992 mol of formaldehyde, which confirmed the work of Dixon.

However, in the presence of condensing agents, the experimental values for  $W$  and  $F$  were no longer in such a simple ratio.  $W$  varied from 1.31 to 1.86, and  $F$  varied from 0.15 to 0.47. Therefore, some further reaction involving the splitting out of more water and less formaldehyde must have taken place.

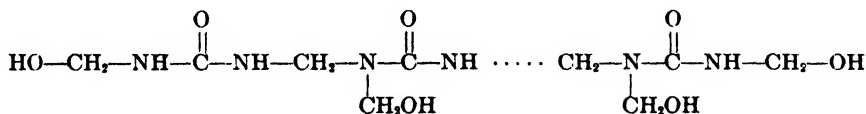
Additional information was provided by a determination of the number of methylene and also the number of methylol groups per urea residue. It is obvious that the number of methylene or methylol groups must be equal to twice the number of urea residues minus the number of escaped formaldehyde molecules.

If  $N$  indicates the number of urea residues per mol of condensation product,  $W$  the escaped water (per urea residue),  $F$  the escaped formaldehyde (per urea residue),  $M$  the methylol groups (per urea residue), then it is generally true that  $W = 2 - (M + F)$ . Furthermore, by allowing  $m$  to represent the number of formaldehyde groups per molecule of resin which have not been converted to methylene groups, (i.e., all the formaldehyde in the resin, including free formaldehyde and that bound as methylol groups),

$$m = N(M + F)$$

$$\text{It follows algebraically, } W = \frac{2N - m}{N}$$

For an open chain structure of the type



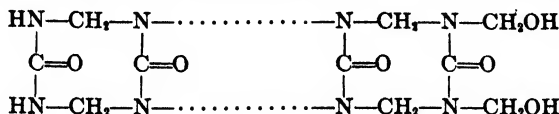
$$\begin{aligned} m &= N + 1 \\ \text{and } W &= \frac{N - 1}{N} \end{aligned}$$

Thus, in considering the limiting case where  $N$  is very large,

$$W = 1$$

This value is incompatible with the analytical data of Walter and Gewing, hence a simple open chain structure is excluded.

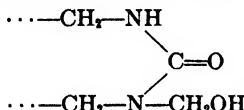
In the case of an open ring chain structure, such as



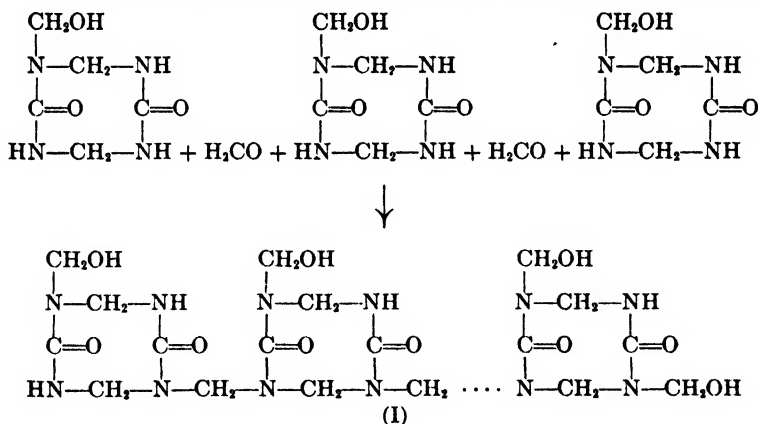
$$m = 2$$

$$\text{and } W = \frac{2N - 2}{N}$$

it can readily be seen that the limiting value for  $W$  in this case is 2. Such a structure for the urea-formaldehyde resins is, therefore, possible provided  $N$  is not excessively large. A variant in which one methylol group is eliminated as formaldehyde leaving the terminal structure in the following form is also possible.



The experimentally determined values of  $W$ , and also the physical properties of the resins, suggest that such a simple ring chain does not completely represent the structure of the high-molecular substances involved. Formulas with ramified chains, however, are more readily compatible both with the quantitative data and the nature of the resinous products. A structure such as the following may be looked upon as being derived from Goldschmidt's compound and formaldehyde.

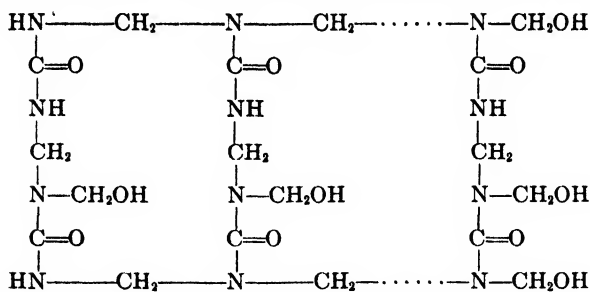


In the formation of Goldschmidt's compound from two dimethylolurea molecules, one formaldehyde molecule is split out. If this formaldehyde is taken up again in the formation of the ramified chain, the net change of formaldehyde would be zero. From the structure given above,

$$M = \frac{N}{2} + 1 \qquad W = \frac{3N - 2}{2N}$$

with the result that  $W$  tends to approach a limit of  $3/2$ . This concept agrees fairly well with the experimentally determined values of  $W$  and  $F$ , already referred to above.

The formation of rings larger than the eight-membered ring hitherto considered is also possible:



$$M = \frac{N}{2} + 2$$

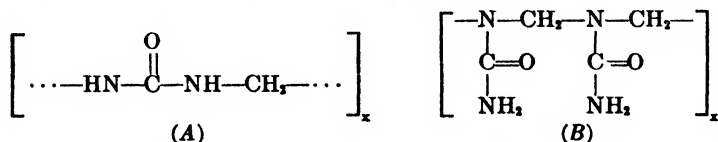
$$W = \frac{3N - 4}{2N}$$

$$\text{Limit of } W = 3/2$$

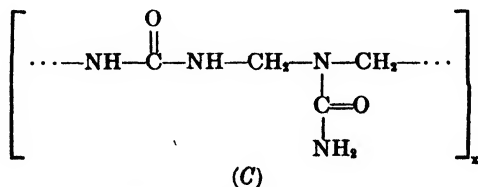
Numerous minor variants of the two preceding types might also be formed, all giving a value for  $W$  in the neighborhood of the values found by experiment. Although the simple chain and ring chain structures are capable of only unidirectional growth, forming linear molecules, the more complex schemes enable condensation to proceed progressively, the methylol groups condensing with the remaining secondary nitrogen atoms of contiguous molecules until the whole becomes knit in a vast ramification of fortuitously arranged three-dimensional networks. The conception may be compared with that holding good for the three-directional ramified, heat-convertible glycerol phthalates (Chapter 41). The values of  $N$  determined by Walter and Gewing were, however, lower than anticipated, the highest value being about 20.

The theory of Walter and Gewing discussed above probably affords a fair representation of the general lines upon which the condensation proceeds, but is not entirely satisfactory. In particular, the nitrogen content of a resin of type (I) would be 30.0 per cent, whereas that of the actual urea-formaldehyde resin, according to Dixon<sup>20</sup> is 32.8 per cent.

If the polymerization be considered as proceeding through the methylolureas, the possible product, starting with monomethylolurea, will be either *A* or *B*, according as the primary or secondary amido-nitrogen is the more reactive.



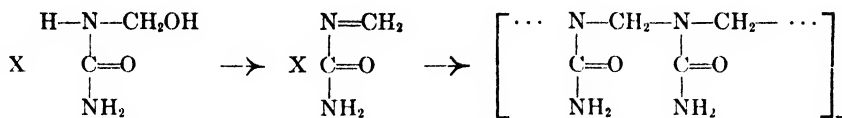
The mixed type *C* is also possible if both nitrogen atoms participate equally in the polymerization.



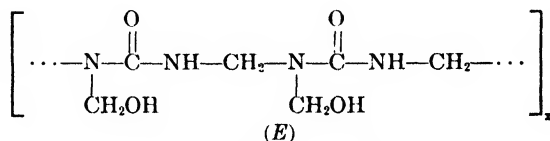
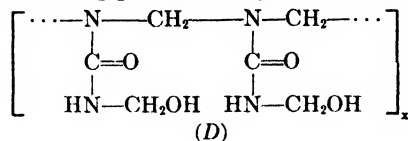
If, on the other hand, polymerization proceeds through initial loss of water leading to the formation of methyleneurea, the product could only be of the type *B*:

<sup>20</sup> A. E. Dixon, *loc. cit.*

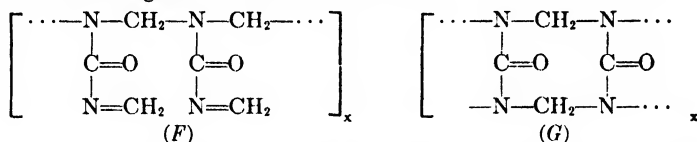




In the case of dimethylolurea, the nature of the products and general considerations indicate that the conditions are essentially similar. Chain formation in this case may be conceived as taking place in two possible ways to yield *D* and *E*,

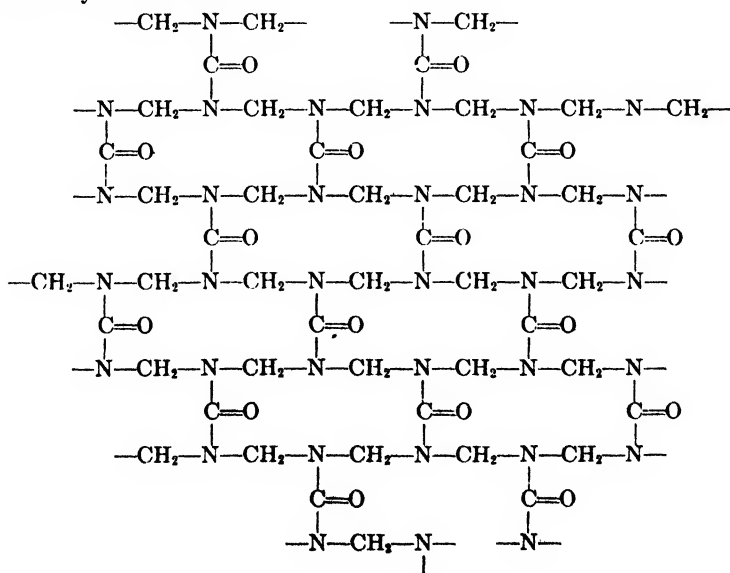


or possibly mixed types as before. Since branching may occur at every methylol group, the formation of long straight chain polymers is improbable. If, now, the remaining methylol groups eliminate water giving methylene groups, *F*, a redistribution of valencies gives the double chain *G*



The chain *D* contains 27.4 per cent nitrogen, whereas *F* and *G* contain 33.3 per cent which compares favorably with the value 32.8 per cent found by Dixon.

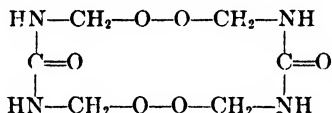
As has been stated, in the actual condensation process chain branching is inevitable, so that the cured resin, if perfectly oriented, could be represented in the simplest case by the formula:



The outer unsaturated valencies would be attached, in the case of the nitrogen atoms to hydrogen, and in the case of methylene groups, to hydroxyl. It may be that the acid or basic radicals of catalysts or fillers are chemically attached to these bonds.

De Chesne<sup>22</sup> arrived at a similar mechanism for the condensation of urea and formaldehyde. His views are based chiefly on the work of Scheibler and Walter, but he has concluded rather that the ultimate product consists of linear polymeric molecules possessing one-dimensional extension only, after the type of the polyoxymethylenes. The first stage of the condensation is regarded as an addition process, the products of addition being mono- and dimethylolurea, which may be isolated by checking the subsequent process of polymerization. A further intermediate step was represented by a crystalline soluble substance melting at 156°C., which cannot, however, have been homogeneous since de Chesne found it to have a variable composition. At every stage beyond the initial formation of dimethylolurea, the condensed mass consists invariably of the complex mixture of ill-characterized, non-separable substances representing a variety of stages in a progressive polymerization process.

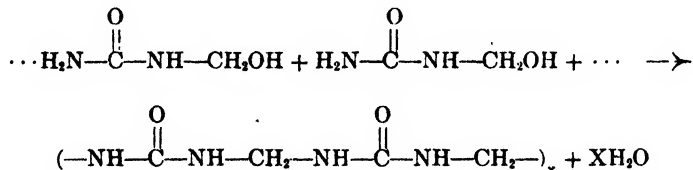
The oxidative degradation of the resin at various stages of the polymerization, using a mixture of concentrated nitric acid and 40 per cent hydrogen peroxide led to the formation of soluble products, from which a crystalline compound was isolated by de Chesne. Analysis of this product indicated the formula,  $C_6H_{12}O_6N_4$ ; hence, it would seem to be a dimethylolurea peroxide having the probable structure



and is apparently identical with that obtained by Girsewald and Siegens<sup>23</sup> who employed peroxide oxidation during the condensation of urea and formaldehyde. The oxidative degradation of urea-formaldehyde resin evidently effects a complete decomposition to give the starting materials.

Examination of numerous high-molecular substances by the methods of x-ray crystallography has shown them to possess a microcrystalline structure, but in the present instance de Chesne found urea-formaldehyde resin to be completely amorphous.

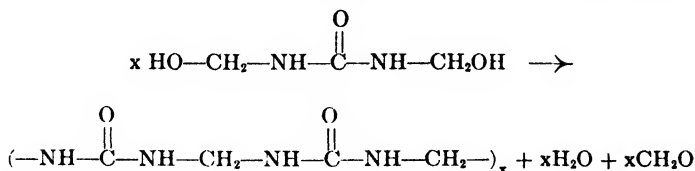
The mechanism of polymerization envisaged by de Chesne is the preliminary formation of methylolurea, or if the  $p_H$  of the reaction mixture be greater than 7, dimethylolurea. Methylolurea then undergoes linear condensation with elimination of water:



Dimethylolurea, in the alkaline reaction mixtures, condenses to the same product, formaldehyde and water being split out simultaneously:

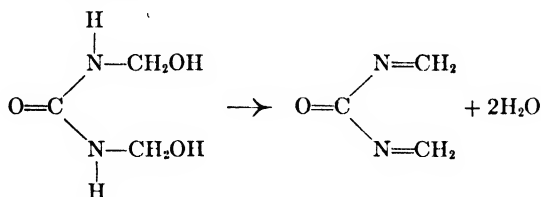
<sup>22</sup> E. B. de Chesne, *Kolloid-Beihfte*, 1932, 36, 387; *Chem. Abs.*, 1933, 27, 459.

<sup>23</sup> C. von Girsewald and H. Siegens, *Ber.*, 1914, 47, 2467.

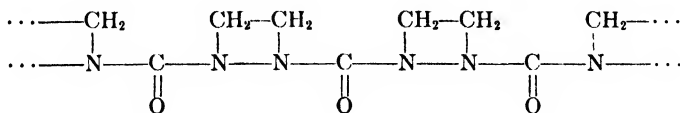


The intermediate stages of the polymerization form highly viscous solutions, which according to de Chesne, display the properties of a highly solvated micelle-colloid. Thus, the high viscosity of the solutions is diminished greatly on heating, and returns to its former value on cooling, whereas molecular colloids show a relatively low temperature variation of viscosity. Moreover, the solutions do not obey the Hagen-Poiseuille law. The conclusion is drawn by de Chesne that the urea-formaldehyde resins consist of micellar aggregates of linear thread-like molecules of varying degrees of polymerization, which form highly solvated hydrophilic colloids possessing the property of irreversible gelation.

Another hypothesis concerning the mechanism of formation of urea-formaldehyde resins has been advanced by Redfarn<sup>71</sup> who attributes the resin formation to the polymerization of dimethyleneurea. In accordance with de Chesne's argument, dimethylolurea is first formed by the action of formaldehyde on urea. However, since the condensation is carried out in acid solution it is conceivable that two molecules of water may be eliminated to yield dimethyleneurea.



The reason why earlier investigations do not indicate the formation of such a structure may be that careful buffering of the reaction solutions was not practiced. The presence of dimethyleneurea should be realized at the stage where the first violent reaction has subsided. Further heating, then, results in polymerization, just as one would expect; the polymer being represented by Redfarn as a saturated chain.



In actual practice the heating is stopped when a thick, viscous syrup is obtained. After addition of fillers, the product is dried at gentle heat whereupon the syrup sets to a resin. This step is considered as the initial process of mutual saturation of the free end valences by ring formation. The saturation, then, is completed during the molding process.

According to Badarelli,<sup>72</sup> the urea-formaldehyde condensation products, especially those derived from thiourea, possess the properties of proteins, and should strictly be classed as artificial albumenoids rather than as synthetic resins.

<sup>71</sup> C. A. Redfarn *British Plastics*, 1933, 5, 238; *Chem. Abs.*, 1934, 28, 1555.

<sup>72</sup> I. Badarelli, *Rev. gen. mat. plastiques*, 1933, 9, 152; *Chem. Abs.*, 1933, 27, 3563.

## Chapter 27

### Urea Resins

#### I. Glass-Like Products. Castings

As has been already indicated in Chapter 26, urea and aqueous formaldehyde, that is, ordinary formalin, can be made to condense to a syrupy solution giving under some conditions a clear glass-like mass on evaporation. Since 1919, this reaction has been studied by chemists the world over in an endeavor to make a substitute for glass. Among the difficulties arising in the course of this work was the lack of permanency of the simulated glass prepared in this manner. For one thing, it was difficult to produce the so-called glass in a form which would be completely resistant to water. The urea-formaldehyde condensate, even when well dried, has a tendency to absorb moisture from the air in a humid atmosphere and to give it out again in dry air. During this "breathing," some action on the surface of the product may occur resulting in a variable dimming of the luster of the material. Furthermore, beautiful specimens of clear glass-like urea resins on standing for some time will almost inevitably form cracks and fissures because of changes in chemical structure (possibly with the elimination of water and formaldehyde) which create stresses and strains (see Fig. 90).

Of course, in articles designed for immediate and short-lived use, lack of permanency is not a handicap, but the flaws that may appear are detrimental in articles made to be kept and used over long periods of time. It has been found, however, that the presence of a filling material of the nature of cellulose fiber minimizes the stresses inherent in urea resins (see Chapter 28), and hence a molding industry of great importance has been established producing urea articles containing usually from 30-40 per cent of cellulose filler. Naturally, the addition of the filler destroys the product's transparent, glass-like appearance, but, on the other hand, thin molded articles containing the added cellulosic material are quite translucent. This translucent effect gives a depth or richness of appearance which would be difficult to equal with phenol-formaldehyde molded products.

#### THE UREA-FORMALDEHYDE CONDENSATION

John<sup>1</sup> prepared a glue by reacting urea or some of its derivatives (e.g., acetyl-urea) and an excess of formaldehyde at a relatively high temperature without adding a condensing agent. Thus, 5 parts of 40 per cent formalin are heated with 1 part of urea until nearly half of the liquid has been removed by distillation. The glue obtained is highly adhesive and adheres in the cold state to glass and metals. It may be admixed with pigments and is suggested for use in filling root canals (in dentistry) and as an impregnant for fabrics. The reaction product can be hard-

<sup>1</sup> H. John, U. S. P. 1,355,834, Oct. 19; 1920; *Chem. Abs.*, 1921, 15, 418. British P. 151,016, 1920; *Chem. Abs.*, 1921, 15, 1606. For a review of the development and characteristics of urea-formaldehyde resins, see J. Taylor, *Australian Plastics and Allied Trades Rev.*, 1933, 2 (2), 8; *Chem. Abs.*, 1934, 28, 661. For a brief review of the early literature, see W. Herzog, *Tech.-Ind. Schweiz. Chem. Ztg.*, 1924, 240, and A. E. Dixon, *J.C.S.*, 1918, 113, 238. See also J. Frère, *Kunststoffe*, 1925, 15, 92.

ened by heating to 80°C. By varying the method of procedure, John also obtained glass-like products.<sup>2</sup> In a gelatinized form, the material may be used as a substitute for rubber.

Goldschmidt and Neuss<sup>3</sup> added controlled amounts of acids or acid salts (not more than 0.5 per cent of the quantity of urea) during the condensation of the reactants. The coagulating effect of acids on the condensate had already been noted by Girsewald and Siegens.<sup>4</sup>

The proportion of formaldehyde necessary to produce clear resins is materially reduced by additions of acid condensing agents. Thus, by heating 100 g. of 30 per cent formalin with 20 g. of urea and 0.013 g. of hydrochloric acid at 100°C., a transparent product which hardens on prolonged heating is obtained. In case a glass-like transparency is not essential, the proportion of formaldehyde may be further lowered. If only 90 g. of formaldehyde solution are used, a milk-white resin is produced. Further reductions in the amount of formaldehyde and the use of larger quantities of acids result in the formation of porous masses resembling meerschäum.<sup>5</sup> As an example, 20 g. of urea are dissolved in 60 g. of 30 per cent formalin, with an addition of 20 g. of water, and heated until foaming occurs. If 5 g. of concentrated nitric, sulphuric or hydrochloric acid are then added, a strongly exothermic reaction takes place giving a porous mass upon cooling. Increase in the proportion of formaldehyde leads to the formation of a harder resin; a decrease, on the other hand, gives rise to a softer product. Ivory-like castings are formed by molding urea-aldehyde compositions in the presence of sulphuric acid.<sup>6</sup>

By adding formalin to fused urea, Neuss<sup>7</sup> obtained a chalky, porous, opaque substance. The urea (100 g.) is heated until molten, and 200 g. of a 40 per cent formaldehyde solution are added. A condensing agent, 4 g. of concentrated sulphuric acid, is introduced with the melted urea at the same time. The chalky reaction product, when washed, dried and hot-pressed, yields a horny, compact material. On heating 1 mol of urea with 3 or more mols of formaldehyde in the presence of a small amount of hydrochloric acid, Rothera, Blythen and Gillespie<sup>8</sup> obtained a gelatinous liquid which solidified when cooled.

Mittasch and Ramstetter<sup>9</sup> found that glass-clear products could be prepared by heating urea with at least 2.4 mols of formaldehyde in the presence of dilute mineral acids (e.g., nitric or phosphoric acids) or of acid salts. Alternatively, organic acids (oxalic, tartaric or acetic acid) may be used as condensing agents.<sup>10</sup> In the production of transparent resins, it has been found advantageous, in order to obtain stable bodies, to effect condensation under conditions of rigidly controlled acidity. By the use of buffer mixtures<sup>11</sup> (e.g., potassium hydrogen oxalate, mono- or disodium phosphate or citric acid and sodium citrate) the acidity is held between the pH limits 4 to 7. If water be then removed by evaporation at a temperature below 50°C., the solution may be considerably concentrated without premature gelation. The product may be hardened at 60-80°C. As an example of the use of this method, a warm concentrated solution of 6 parts of urea, containing 0.11 part of monosodium phosphate and 0.04 part of disodium phosphate is slowly

<sup>2</sup> See also D. Beck (Swiss P. 92,984, 1921) who condensed formaldehyde polymers with urea.

<sup>3</sup> H. Goldschmidt and O. Neuss, British P. 208,761, 1922; *Chem. Abs.*, 1924, 18, 1555.

<sup>4</sup> C. von Girsewald and H. Siegens, *Ber.*, 1914, 47, 2465; *Chem. Abs.*, 1915, 9, 77.

<sup>5</sup> H. Goldschmidt and O. Neuss, U. S. P. 1,844,570, Feb. 9, 1932, to Synthetic Plastics Co., Inc.; *Chem. Abs.*, 1932, 26, 2073. British P. 187,605, 1922; *Chem. Abs.*, 1923, 17, 1115. German P. 412,614, 1925.

<sup>6</sup> Swiss P. 126,827, 1926, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1929, 23, 942.

<sup>7</sup> O. Neuss, U. S. P. 1,914,937, June 20, 1933; *Chem. Abs.*, 1933, 27, 4362. British P. 372,847, 1932; *Chem. Abs.*, 1933, 27, 3569. British P. 379,154, 1932; *Chem. Abs.*, 1933, 27, 4111. German P. 484,972, 1922, to Kunstharzfabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1930, 24, 1190. German P. 604,194, 1934; *Chem. Abs.*, 1935, 29, 855.

<sup>8</sup> W. S. Rothera, S. Blythen and H. R. Gillespie, German P. 563,037, 1921; *Chem. Abs.*, 1933, 27, 1113. Cf. German P. 568,639, 1921; *Chem. Abs.*, 1933, 27, 2771.

<sup>9</sup> A. Mittasch and H. Ramstetter, German P. 409,847, 1922, to Badische Anilin- & Soda-Fabr.; *J.S.C.I.*, 1925, 44, 462B.

<sup>10</sup> A. Mittasch and H. Ramstetter, German P. 535,851, 1922, addn. to 409,847, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1403.

<sup>11</sup> British P. 258,289, 1926, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1928, 376.

poured into 25 parts of boiling 30 per cent formaldehyde. The product is evaporated *in vacuo*, at a temperature below 50°C., to a syrupy consistency, containing 10-15 per cent of water, and is stable for a considerable time. It may be cast in molds and hardened for 1 or 2 days at 65°C. without loss of clarity.

After effecting condensation at a  $p_H$  of 4-6 the  $p_H$  may be raised to 6-7 before concentration.<sup>12</sup> Clear products may be thus formed using a smaller proportion of formaldehyde than is otherwise possible. If a smaller molar ratio (1.5-1.7 mols of formaldehyde to 1 of urea) is used, evaporation may be partly or entirely dispensed with,<sup>13</sup> since the resin separates on cooling. The addition of salts (sodium sulphate) during the latter process is also suggested.

Knilling<sup>14</sup> fused urea and solid polymers of formaldehyde with the addition of small quantities of mild alkaline condensing agents (organic compounds giving an alkaline reaction) or sodium acetate and borax. Clear, colorless melts result which furnish white or glass-like masses according to the conditions of the subsequent hardening treatment. An intimate mixture of 200 parts of urea, 52 parts of thio-



FIG. 90.—Formation of Cracks in Clear Urea-Formaldehyde Resins.

urea (the addition of thiourea increases the transparency of the product), 240 parts of trioxymethylene, 6 parts of sodium acetate and 20 parts of formamide<sup>15</sup> is heated in an oil bath at 140°C. for about 20 minutes. The melt becomes viscous and is transformed on cooling into a hard, white mass which may be reduced to a fine powder. The powdered material is suggested for use as a waterproof adhesive in veneering wood.

Pollak<sup>16</sup> also described the use of alkaline condensation catalysts, using weak bases (pyridine, ammonia and hexamethylenetetramine). In the presence of these substances as catalysts, urea, heated with not more than 3 mols of formaldehyde, gives, after partial evaporation, a syrup which sets at 75°C. to a hard, transparent mass (sp. gr. 1.3) which is insoluble in both alkalies and acids. The cast resin undergoes carbonization at 300°C. without melting, and may be machined and turned. If condensation is first effected in the presence of a large excess of formaldehyde, that excess must be removed before the hardening step. The syrupy, partially condensed product may be used for impregnating porous material, and may

<sup>12</sup> British P. 288,246, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 678.

<sup>13</sup> M. Luther and C. Heuck, German P. 537,611, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1404.

<sup>14</sup> W. von Knilling, U. S. P. 1,920,451, Aug. 1, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4890. British P. 314,908, 1923; *Chem. Abs.*, 1930, 24, 1711. German P. 600,678, 1934; *Chem. Abs.*, 1934, 28, 7443.

<sup>15</sup> The properties of formamide are discussed by P. L. Magill, *Ind. Eng. Chem.*, 1934, 26, 611.

<sup>16</sup> F. Pollak, U. S. P. 1,458,543, June 12, 1923; *Chem. Abs.*, 1923, 17, 2632. British P. 171,094, 1921; *Chem. Abs.*, 1922, 16, 995.

be mixed with mineral or cellulosic fillers. By incorporating dyes, substitutes for amber, coral, tortoise shell and mother of pearl are reported to be produced.

Oxides and carbonates have been suggested as condensing agents by several investigators.<sup>17</sup> Thus Barthélemy<sup>18</sup> used the carbonates of magnesium and the alkaline earths as condensing agents to bring about the union of urea and formaldehyde beyond the stage of methylolurea formation. On boiling 60 parts of urea with 200 parts of 30 per cent formaldehyde, with the addition of 6 per cent by weight of freshly precipitated calcium carbonate, a syrup is obtained which may be concentrated *in vacuo* to a hygroscopic, amorphous extract or a water-soluble gum, which behaves as a reversible colloid in contact with aqueous solutions of  $p_H$  8.6-10. By the addition of acid, whereby the  $p_H$  is changed to any value below 4, gelation of the gum takes place, yielding a horny mass which becomes transparent, and may be worked or polished on drying. Other heavy metal carbonates<sup>19</sup> (e.g., zinc or lead carbonate) and also the corresponding oxides (such as titanium oxide) catalyze the initial condensation. The use of these condensing agents has the advantage that the catalyst is rapidly removed completely by filtration, and the resulting products are desiccated with greater readiness. In addition, colored metallic carbonates (e.g., copper carbonate) serve as pigments for the resin.

Hydrogen peroxide was employed by Geisel<sup>20</sup> in the condensation of urea and formaldehyde at raised temperatures. The hydrogen peroxide (1 part of a 30 per cent solution) is stirred, with 44 parts of urea dissolved in an equal amount of water, into 196 parts of commercial formalin at a temperature of 70°C. As soon as reaction begins, the mixture is heated for a half hour at 100°C., after which it is concentrated *in vacuo* to a viscous liquid. On cooling, a clear, transparent mass is obtained.

According to Ramstetter,<sup>21</sup> both the condensation process and the curing process are accelerated by exposure of the resin to ultraviolet radiation from a quartz mercury arc lamp, the products under these conditions being harder, tougher and more resistant to water. The clouding tendency during the curing stage is also reduced or suppressed thereby.<sup>22</sup>

Kadowaki and Hashimoto<sup>23</sup> state that the optimum temperature for condensation is 85°C. and that the best results are obtained by adding the urea solution to the solution of formaldehyde. By drying the product at 60°C. and then at 100°C., the formation of gas bubbles may be avoided, although the investigators state that the resin tends to crack upon standing. Furthermore, it cannot be cast on account of shrinkage, and the thickness of resin stock obtainable is limited. These defects are reported to be overcome by hot molding during which the powdered condensation product is heated at 120°C. under 60 atmospheres pressure. As condensing agents, Kadowaki and Hashimoto advocate either weak inorganic acids, inorganic or organic bases or the salts of alkali and alkaline earth metals with organic acids.

Howald<sup>24</sup> produced a resin derived from ammonium cyanate. The ammonium cyanate (1 mol) is refluxed with 2 mols of the aldehyde (formaldehyde or acetaldehyde), the solution being kept neutral or slightly alkaline. The water is next removed, and fillers and plasticizers are added while the solution is still viscous. The mixture is dried, powdered, a fixing agent (urea or thiourea) for formaldehyde is added and the product is molded.

<sup>17</sup> See also Chapter 28.

<sup>18</sup> H. Barthélemy, U. S. P. 1,645,848, Oct. 18, 1927, to Soc. ind. des mat. plastiques; *Brit. Chem. Abs. B*, 1927, 916.

<sup>19</sup> J. Malet and R. Armenault, French P. 679,321, 1928, to Fabr. de prod. de chim. org. de Laire; *Chem. Abs.*, 1930, 24, 3914. British P. 340,114, 1928; *Chem. Abs.*, 1931, 25, 2822. U. S. P. 2,004,996, June 18, 1935.

<sup>20</sup> W. Geisel, German P. 493,988, 1924, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2846.

<sup>21</sup> H. Ramstetter, German P. 416,352, 1923, to Badische Anilin- & Soda-Fabr.; *Brit. Chem. Abs. B*, 1926, 90.

<sup>22</sup> W. Geisel, German P. 437,646, 1924, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1927, 452.

<sup>23</sup> H. Kadowaki and Y. Hashimoto, *Repts. Imp. Ind. Research Inst. Osaka (Japan)*, 1926, 7 (6), 1; *Chem. Abs.*, 1926, 20, 3541.

<sup>24</sup> A. M. Howald, U. S. P. 1,928,492, Sept. 26, 1933, to Toledo Synthetic Products, Inc.; *Chem. Abs.*, 1933, 27, 5996. Canadian P. 328,910 and 328,912, 1933; *Chem. Abs.*, 1933, 27, 1531.

## THE PREPARATION OF METHYLOLUREAS

The investigations of Einhorn and Hamburger,<sup>24</sup> on the formation of monomethylolurea and dimethylolurea by condensing urea and formaldehyde in the presence of barium hydroxide have been discussed in Chapter 26.

To obtain dimethylolurea, they added 10 g. of urea to a solution containing 0.4 g. of barium hydroxide in 26.7 g. of 37.4 per cent formalin (2 mols of formaldehyde) and maintained the mixture at 25-30°C. until all the formaldehyde had reacted. The end-point of the reaction can be determined by Tollen's reagent (equal volumes of a 10 per cent solution of ammoniacal silver nitrate and a 10 per cent aqueous sodium hydroxide solution) which does not give a precipitate in the absence of formaldehyde. Carbon dioxide is then introduced at once to counteract the alkalinity of the barium hydroxide. The resulting liquid is dried in a desiccator without removing barium carbonate and the residue is extracted with warm 80 per cent alcohol. By cooling the filtered solution, 8 g. of dimethylolurea crystallizes out, and an additional 2 g. may be obtained by further cooling the mother liquor.

Monomethylolurea can be obtained, according to Einhorn and Hamburger, by slowly dropping 6.5 cc. of 37.4 per cent formalin into an ice-cooled solution of 5 g. of urea and 0.1 g. of barium hydroxide in 5 cc. of water followed by the immediate addition of carbon dioxide. The solution is filtered and evaporated in a desiccator, yielding the product as a crystalline mass.

Dimethylolurea is soluble in cold water and in warm methyl or ethyl alcohol, but is insoluble in ether and most other organic solvents. On heating, it sinters at 121°C. and melts at 126°C. forming a clear liquid which changes at 137-138°C. into an amorphous white material that does not melt on further heating but decomposes at 260°C. When dimethylolurea is heated in a test tube, the odor of formaldehyde and basic decomposition products is noted. The compound (in aqueous solution) gives a white amorphous precipitate on standing for several hours with dilute mineral acids.

Monomethylolurea, however, gives a flocculent amorphous precipitate almost instantly with dilute mineral acids and acetic acid. Cold water and methyl alcohol also dissolve monomethylolurea. Dimethylolurea reduces Tollen's reagent after some time, but monomethylolurea gives no formaldehyde reaction with sodium nitroprusside or phenylhydrazine.

Methylolurea or methylolthiourea and methylol derivatives of other acid amides may be prepared by the interaction of formaldehyde and the amide in non-aqueous solvents,<sup>25</sup> e.g., methyl or ethyl alcohol. The condensation is accelerated by basic substances, and the product may be precipitated by the addition of ether or carbon tetrachloride. By rapidly melting the compounds formed in this manner, with the addition of urea or thiourea and of acids (e.g., acetic acid) and buffer salts, clear or opaque resinous masses are obtained. In the preparation of dimethylolurea, the use of solvents in which the substance is not very soluble is advantageous, and formaldehyde polymers may be substituted for non-aqueous formaldehyde.<sup>26</sup> The methylol compounds of other acid amides (e.g., methylolacetamide) are similarly obtained.<sup>27</sup>

Dimethylolurea is also made<sup>28</sup> in aqueous, neutral or mildly alkaline solution

<sup>24</sup> A. Einhorn and A. Hamburger, *Ber.*, 1908, 41, 24. A. Einhorn, *Ann.*, 1908, 361, 113.

<sup>25</sup> G. Walter, *British P.* 262,145, 1925; *Chem. Abs.*, 1927, 21, 3626.

<sup>26</sup> G. Walter, *British P.* 284,373, 1925; *Chem. Abs.*, 1928, 22, 4538. German P. 519,322, 1926; *Chem. Abs.*, 1932, 26, 5163.

<sup>27</sup> G. Walter, *British P.* 291,712, 1926; *Chem. Abs.*, 1929, 23, 1136. Austrian P. 130,030, 1930; *Chem. Abs.*, 1933, 27, 1001.

<sup>28</sup> M. Schmhing, U. S. P. 1,969,628, Jan. 29, 1935, to Unyte Corp.; *Chem. Abs.*, 1935, 29, 1836. *British P.* 368,027, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3163. French P. 721,828, 1931; *Chem. Abs.*, 1933, 26, 4067. German P. 558,945, 1933; *Chem. Abs.*, 1934, 28, 2020.



(e.g., 0.02-0.005 *N* caustic soda)<sup>29</sup> by concentration of the solution at a low temperature immediately after the reacting urea and formaldehyde are brought together.

The formation of dimethylolurea may be brought about at room temperature by the catalytic action of active carbon (e.g., a suspension of animal charcoal); pure and stable dimethylolurea is reported to result on evaporation after filtration from the carbon.<sup>30</sup> By heating the mixture under reflux, condensation proceeds further, yielding syrups of progressively increasing viscosity and decreasing solubility. These may be concentrated *in vacuo* to a material which solidifies to a clear, hard resin on prolonged heating at 60-100°C. This further condensation is retarded by the addition of alcohols, ketones, ethers or esters to the mixtures and reaction may be checked at any stage by such addition. The retarding agents are useful in preventing prematurely complete polymerization when condensation is effected in the presence of acids. The effect of retarding agents may be illustrated by an example cited by Gams and Widmer, in which 240 parts of urea are dissolved in 660 parts of 36 per cent formaldehyde, and 200 parts of ethyl alcohol added. The mixture is shaken with animal charcoal, filtered and boiled under a reflux condenser after adding 0.24 part of concentrated phosphoric acid in 20 parts of water. After several hours boiling, the liquid is still miscible with water and yields, on evaporation, a resinous syrup. In the absence of alcohol, the condensation of this mixture would proceed rapidly to completion.

#### POLYMERIZATION OF METHYLOLUREAS

Walter<sup>31</sup> found that glass-clear, transparent resins are obtained from monomethylolurea (m. p. 111°C.) and dimethylolurea (m. p. 126°C.) by rapidly melting the substances and maintaining them in the molten state, but below 140°C., until the mass, though viscous, may still be cast. Water and formaldehyde are thereby eliminated. The addition of fluxing agents, by lowering the melting point of the methylolurea, permits slower heating and eliminates much trouble due to frothing. Neutral and alkaline salts (e.g., calcium chloride or sodium acetate) or neutral mixtures of salt and acid (e.g., sodium acetate and glacial acetic acid) are satisfactory for this purpose, as also are urea, methylolamides and phenols. The addition of paraformaldehyde promotes the elasticity and flexibility of the product. With monomethylolurea, up to equimolecular proportions may be added, the use of acid fluxing and stabilizing agents being then desirable.

As an example of this process, 200 parts of paraformaldehyde are dissolved in a solution of 5 parts of caustic soda in 1100 parts of 94 per cent alcohol, and 200 parts of urea are added to the cold solution. After a few hours, the deposit of dimethylolurea may be separated. The dimethylolurea, when rapidly fused, undergoes violent foaming. If about 0.3 per cent by weight of chloroacetic acid be added to the clear melt, the mass rapidly thickens and may be cast in molds. Similarly, monomethylolurea containing about 2 per cent of sodium acetate may be fused after adding 1 per cent of caustic soda dissolved in a little water. The melt clears and finally gelatinizes, giving a glass-clear product which may be pulverized and molded under pressure at elevated temperatures.

According to Walter,<sup>32</sup> the polymerization of dimethylolurea or its mixtures with monomethylolurea, may be brought about by alkalies, giving as products resinous materials for molding compositions or lacquer ingredients. The polymerization is performed in the absence of substantial amounts of solvents, e.g., by mixing

<sup>29</sup> E. C. C. Baly and E. J. Baly, British P. 299,437, 1927, to Pollopos, Ltd.; *Chem. Abs.*, 1929, 23, 3236. French P. 656,285, 1928; *Chem. Abs.*, 1929, 23, 4090.

<sup>30</sup> A. Gams and G. Widmer, U. S. P. 1,676,543, July 10, 1928, to Soc. anon. pour l'ind. chim à Bâle; *Chem. Abs.*, 1928, 22, 3369. Canadian P. 274,268, 1927; *Chem. Abs.*, 1927, 21, 3907. British P. 253,094, 1925; *Chem. Abs.*, 1927, 21, 2539.

<sup>31</sup> G. Walter, U. S. P. 1,863,426, June 14, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4142. Austrian P. 180,002, 1928; *Chem. Abs.*, 1933, 27, 1113. German P. 512,566, 1926; *Chem. Abs.*, 1933, 27, 857. British P. 262,143, 1926; *Brit. Chem. Abs. B.*, 1928, 614.

<sup>32</sup> G. Walter, Austrian P. 121,999, 1930; *Chem. Abs.*, 1931, 25, 3185. Austrian P. 123,847, 1931; *Chem. Abs.*, 1931, 25, 5585.

dimethylolurea and monomethylolurea with 1-7 per cent by weight of caustic soda, either solid or in concentrated solution, and heating to 110-130°C. The products are hardened by heat and pressure.

In non-aqueous solvents such as ethyl alcohol, owing to the insolubility of the products, coupled with the decreased ionization of the alkalies, the action of strong alkaline condensing agents leads to the formation of mono- or dimethylolurea, without subsequent polymerization.<sup>33</sup> Anhydrous formaldehyde may be used in the form of trioxymethylene or paraformaldehyde. Thus, 130 parts of trioxymethylene are dissolved in 316 parts of methanol in the presence of 3 parts of 50 per cent caustic potash solution. To this are added 12 parts of caustic potash solution and 152 parts of thiourea. After a short time, resinous dimethylolthiourea precipitates and can be separated, washed with acetone and pulverized. Methylolurea or methylolthiourea so obtained may be fused rapidly and treated with a small quantity (not more than 1 per cent) of caustic alkali, whereupon the mass thickens and gelatinizes, finally setting to an opalescent product.

The separation of methylolurea in the solid form is not proposed if unmodified urea-formaldehyde resins are required. It is possible, alternatively, to effect preliminary condensation as far as or beyond the stage of methylolurea formation, then to polymerize the first condensation products by the addition of acid. A process of this nature has been described by Ripper.<sup>34</sup> The first stage of condensation must occur in neutral solution, e.g., by adjusting the  $pH$  to a value not lower than 7. Should the acidity rise above this value, white precipitates are produced which lead inevitably to the ultimate formation of a clouded or opaque resin. At a  $pH$  of 7, however, a water-clear solution is obtained, even with as little as 2 mols of formaldehyde per mol of urea. On cooling, cloudy solutions are formed which clear on heating, and on prolonged boiling yield viscous masses which harden to clear resins. In working by this process, either so-called acid-free formaldehyde may be used (e.g., that obtained by subliming the solid polymers in the absence of air) or ordinary formaldehyde may have its formic acid neutralized by addition of a base. The polymerization of the condensed substance may be brought about either by lengthy heating, or more expeditiously, by addition of sufficient acid to raise the  $pH$  to about 3. For this purpose, acid salts, acid esters or ammonium salts may be added. The latter function by reacting with formaldehyde to form hexamethylenetetramine, liberating the acid. Alternatively, formic acid may be formed *in situ* by aerating the mass. The acidity during polymerization should not rise above a  $pH$  of about 2.6 (corresponding to an amount of sulphuric acid less than 0.017 per cent of the urea employed), since gelation then occurs instantly, forming a hard, white, brittle material (containing all the water) which on standing loses water by evaporation, and becomes clear but readily crumbles to a powder.

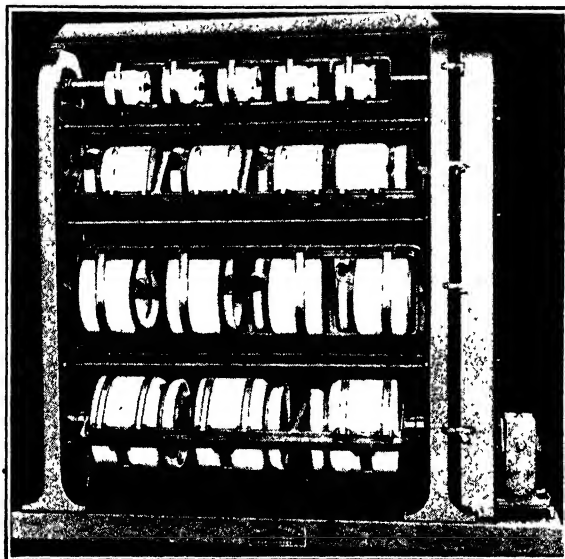
By this process, 30 parts of urea are condensed by refluxing for a short time with 100 parts of neutral 30 per cent formaldehyde. Five parts of boric acid, dissolved in a little water, are added, and the mixture boiled for a further period. After 2.5 hours, the reaction mixture is converted into a moderately viscous solution which does not become cloudy on cooling, and which marks the polymerization of the initially formed methylolurea material into a colloidal hydrophilic sol. This may be hardened by evaporating most of the water, casting in molds and heating at 60-100°C. to give a transparent final product. More prolonged boiling of the mixture (6-7 hours) carries polymerization further, the clear, hot solution then depositing on cooling a white, slimy jelly from which the supernatant liquid may be decanted. The jelly, which is opaque due to adsorbed water, may be dried *in vacuo*, thereby being rendered transparent. It may then be cast in molds and cured. Boric acid may be

<sup>33</sup> G. Walter, U. S. P. 1,863,426, June 14, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4142.

<sup>34</sup> K. Ripper, U. S. P. 1,687,312, Oct. 9, 1928, to F. Pollak; *Chem. Abs.*, 1928, 22, 4739. British P. 213,567, 1923; *Chem. Abs.*, 1924, 18, 2412. W. S. Rothera, S. Blythen and H. R. Gillespie, German P. 589,726, 1923; *Chem. Abs.*, 1932, 26, 2286.

replaced as a polymerizing agent by other acids, e.g., by adding 0.13 part of acetic acid, 1 part of ammonium acetate, 0.1 part of benzoic acid or a trace (of the order of 0.0005 part) of sulphuric acid.

Gams and Widmer<sup>38</sup> have described the preparation of porous materials of improved mechanical strength, free from electrolytes, by a process of initial condensation in neutral solution somewhat beyond the stage of dimethylolurea, followed by polymerization on the addition of a sufficient quantity of acid. A solid jelly is obtained which rapidly becomes white and hard and from which the catalyst may be eliminated by osmosis or, more rapidly, by electro-osmosis. If an acid catalyst is employed, it is removed by neutralizing and then washing the resulting



Courtesy Paule O. Abbé, Inc.

FIG. 91.—Combination Jar Mill.

salt. The specific gravity of the product may be as low as 0.4, if much solvent has been used. The application of high pressures increases the strength and density of the materials. The hardness of the product is governed by the nature and the proportion of the catalyst used, and may be further modified by the addition of softening agents, e.g., triphenyl phosphate, diethyl phthalate, linseed oil or latex. Fillers (e.g., cellulose and asbestos) and materials capable of taking part in the resin formation (phenol) may also be added. The products are characterized by considerable mechanical strength, toughness and good insulating properties. They may be machined and worked.

A process for the coagulation of the primary condensation product, described by Ripper,<sup>39</sup> depends on the flocculation of the substances from very dilute solution by further addition of solvent or by the use of flocculants (acids, bases or albumin precipitants such as phosphotungstic acid). No gelatinization occurs, but the mate-

<sup>38</sup> A. Gams and G. Widmer, U. S. P. 1,831,706, Nov. 10, 1931, to Soc anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 815. British P. 281,717, 1928; *Chem. Abs.*, 1928, 22, 3747. German P. 523,181, 1926; *Chem. Abs.*, 1931, 25, 3448. French P. 644,648, 1937; *Chem. Abs.*, 1929, 23, 2001.

<sup>39</sup> K. Ripper, U. S. P. 1,907,261, July 24, 1934, to Synthetic Plastics Co., Inc.; *Chem. Abs.*, 1934, 28, 5941. British P. 271,037, 1927, to Kunstharzfabr. Dr. F. Pollak G.m.b.H.; *Brit. Chem. Abs. B.*, 1928, 720. French P. 637,318, 1927; *Chem. Abs.*, 1929, 23, 494. Cf. W. Rothera, S. Blythen and H. R. Gillespie, German P. 539,473, 1927; *Chem. Abs.*, 1932, 26, 1813.

rial is obtained as a white, amorphous powder which may be molded by heat and pressure. The powder is insoluble in water, but soluble in acids, hot formalin and in high-boiling hydroxylic solvents (glycerol). After molding, transparent or translucent resins are obtained which, according to Ripper, may be used as substitutes for crystal, glass or amber.

Porous masses of uniform consistency are formed<sup>77</sup> on gelatinizing the initial condensation product and partially hardening the mass without first concentrating the solution to any considerable extent. A large proportion of a dispersion medium (alcohol) may be added. Gelation may be effected by addition of acids or of ammonium salts. The effect of gelatinizing at high dilutions is to cause retention of the dispersion medium in the pores of the colloid. Since the dispersion medium is evaporated at a low temperature, the porous structure is retained leaving a translucent or meerschäum-like material, according to the pore size.

The gelatinization of the initial condensation product, i.e., the conversion of the hydrophilic to a hydrophobic sol, may also be effected<sup>78</sup> by introducing additional organic compounds capable of resin formation with the formaldehyde (e.g., urea or thiourea). Phenol may also be employed in this connection giving a soft, kneadable resin from which glass-clear masses may be made. The mixture is further heated in the presence of acid and on cooling, after neutralization, the resin precipitates as a viscous mass. The resistance towards water and the insulating properties of the cured resins are greatly augmented by this process.

Thus, 1500 parts of urea are boiled with 4000 parts of neutral 37.6 per cent formaldehyde solution, then 2 parts of formic acid and 300 parts of thiourea or 230 parts of urea (alternatively, 200 parts of phenol) are added. After 2 hours of boiling, the formic acid is neutralized by 2 parts of alkali carbonate, and the mass is cooled. The resin which separates may be repeatedly washed with water and then hardened in molds (being further dried by evaporation below 50°C.) or may be dissolved in 30 per cent of its weight of acetone to give a lacquer.

According to Gams and Widmer,<sup>79</sup> the condensation process may be considerably accelerated by carrying it out at a temperature above 100°C. under pressure, such conditions enabling complete control of the progress of the reaction and the required consistency of the product to be attained. Thus, 600 parts of urea dissolved in 1,645 parts of neutralized 36.5 per cent formaldehyde gave a completely soluble product when heated at 115°C. for 1-2 hours in an autoclave, and after 3-4 hours of heating at 120°C. yielded a clear, gelatinous gum. The same degree of condensation would be reached only after 17 hours heating at atmospheric pressure.

In general, concentration of the reacting mixture is necessary at some stage in order to remove the large excess of water in which resinification takes place. The reaction may, however, be carried out in more concentrated media, solutions containing up to 75 per cent of solid matter<sup>80</sup> being made by dissolving urea in the reagent obtained by the dissolution of the solid formaldehyde polymers in ammonia, alkaline formates and acetates or acids. The formaldehyde content of the solution may exceed 40 per cent. On boiling these concentrated reaction mixtures in an open vessel, viscous condensation products are obtained, hardening at 100°C. to clear, glassy masses.

<sup>77</sup> K. Ripper, U. S. P. 1,779,047, Oct. 21, 1930, to Kunstharsfabr. Dr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1931, 25, 177. *British P.* 261,409, 1925; *Chem. Abs.*, 1927, 21, 3432. *Austrian P.* 111,534, 1928; *Chem. Abs.*, 1929, 23, 1729.

<sup>78</sup> K. Ripper, U. S. P. 1,533,868, Nov. 24, 1931, to Synthetic Plastics Co., Inc.; *Chem. Abs.*, 1932, 26, 1144. F. Pollak, *British P.* 248,729, 1925; *Chem. Abs.*, 1927, 21, 805. K. Ripper, *Canadian P.* 284,790, 1928, to Kunstharsfabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1929, 23, 1001.

<sup>79</sup> A. Gams and G. Widmer, U. S. P. 1,674,199, June 19, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1928, 22, 2818. *British P.* 246,126, 1926; *Brit. Chem. Abs. B.*, 1927, 496. *German P.* 487,871, 1925; *Chem. Abs.*, 1930, 24, 2258. *Canadian P.* 281,325, 1928; *Chem. Abs.*, 1928, 22, 3270.

<sup>80</sup> F. E. K. Steppes, U. S. P. 1,658,359, Feb. 7, 1928, to Traun & Sons; *Chem. Abs.*, 1928, 22, 1220. *British P.* 271,264, 1926; *Brit. Chem. Abs. B.*, 1927, 584.

The polymerization of the initial condensate, which is rapidly catalyzed by very small additions of acid, may be smoothly and slowly brought about by means of acetic anhydride.<sup>41</sup> Spontaneous gelation of the syrupy condensation products on standing may be suppressed, according to Ripper,<sup>42</sup> by the addition of alkali salts of weak acids (e.g., sodium borate or acetate). Solutions so treated harden only slowly on heating, enabling the latter process to be more readily controlled. The effect of the stabilizers may be neutralized by addition of sodium salts of highly ionized acids, which exert a strong accelerating influence. Stabilization of the urea-formaldehyde resins in the fusible jelly-like state is brought about also<sup>43</sup> by the addition of aqueous dispersions of mucilaginous substances (starch, gum tragacanth or karaya gum).

The gelatinization of the water-soluble condensation product which forms an intermediate stage in the resin condensation is accelerated by the addition of electrolytes.<sup>44</sup> This gelatinizing action shown by non-alkaline electrolytes divides salts into two groups. The first group contains electrolytes that rapidly convert the initial soluble product into hardened, insoluble resins. Included in this division are ammonium thiocyanate, ammonium sulphate and, in general, the ammonium salts of strong acids. The second division comprises salts that exert no hardening action, but do accelerate the gelatinization process. The sulphates, chlorides, nitrates and other mineral acid salts of the metals fall into this category, the anion being the active ion. The action is illustrated by the addition of 1 part of potassium sulphate, chloride or thiocyanate to 100 parts of the water-soluble condensation product from 60 parts of urea and 150 parts of 40 per cent formaldehyde. Gelatinization occurs, and water separates from the mass on standing in the cold. If thick articles are hardened in the cold by accelerating salts, the liberation of water in the interior of the mass is apt to cause cracking. This is said to be overcome by building up the mass with a plurality of layers, each being hardened before deposition of the next.

Before proceeding to hardening treatment, any acidity may be reduced by addition of bases or alkaline salts prior to gelatinization.<sup>45</sup> Cloudiness in the hardened material is controlled or prevented by the addition of salts.<sup>46</sup> Thus, after condensation with hexamethylenetetramine as catalyst, the acidity is determined and excess urea added to neutralize the acid as well as to bind free formaldehyde. Resin made in this manner, on molding, yields a cloudy mass, but addition of sodium chloride, sodium silicate, potassium iodide or other salt prior to hardening leads to the formation of transparent masses.

#### ACID HARDENING OF UREA-FORMALDEHYDE RESINS

The hardening step is accelerated by treating the uncured condensation products with weakly acid solutions of  $p_H$  4-7 (disodium phosphate). Hardening of

<sup>41</sup> H. Barthélemy, U. S. P. 1,691,427, Nov. 13, 1928, to Soc. ind. des mat. plastiques; *Chem. Abs.*, 1929, 23, 489.

<sup>42</sup> K. Ripper, U. S. P. 1,460,606, July 3, 1923, to F. Pollak; *Chem. Abs.*, 1923, 17, 2940. German P. 499,792, 1921; *Chem. Abs.*, 1930, 24, 4596.

<sup>43</sup> E. Lionne, U. S. P. 1,901,373, March 14, 1933; *Brit. Chem. Abs. B*, 1933, 1021.

<sup>44</sup> K. Ripper, U. S. P. 1,625,283, Apr. 19, 1927, to F. Pollak; *Chem. Abs.*, 1927, 21, 2054. F. Pollak, British P. 181,014, 1923; *Chem. Abs.*, 1923, 16, 3531. See also F. Pollak and K. Ripper, *Chem.-Ztg.*, 1924, 48, 609, 583; *J.S.C.I.*, 1924, 43, 878B.

<sup>45</sup> K. Ripper, U. S. P. 1,972,110, Sept. 4, 1934, to Synthetic Plastics Co., Inc.; *Chem. Abs.*, 1934, 28, 6537. F. Pollak, British P. 201,906, 1923; *Chem. Abs.*, 1924, 18, 313. British P. 206,513, 1923; *J.S.C.I.*, 1924, 43, 987B.

<sup>46</sup> The clearing action of the salts follows the order of the Hofmeister series of ions with slight variation. This series is based on the order of the ability of salts to coagulate albumin sola. For a constant anion the order of efficacy is:  $Fe^{++}$ ,  $Al^{+++}$ ,  $K^+$ ,  $NH_4^+$ ,  $Cu^{++}$ ,  $Mg^{++}$ ,  $Zn^{++}$ ,  $Ca^{++}$  and  $Na^+$ . With constant cation the anions were found to fall in the order: sulphate, citrate, oxalate, acetate, chlorate, carbonate, nitrate, bromide, cyanide, thiocyanate, iodide and salicylate.

the cast, uncured, gelatinous resin may be performed according to Luther, Griessbach and others<sup>47</sup> by exposing the surface to gaseous sulphur dioxide, or by immersion in an acetone solution of sulphur dioxide. The use of aqueous solutions, which frequently lead to surface opacity, is thus avoided. Products cured with sulphur dioxide are comparatively stable and, in contact with liquids, swell less than urea-formaldehyde resins hardened directly. The treatment with sulphur dioxide may be performed at an elevated temperature, effecting a rapid hardening. Various applications of urea-formaldehyde resins, as in the preparation of non-inflammable artificial fibers, are thus suggested.

In place of sulphur dioxide, other volatile acids may be employed as hardening agents,<sup>48</sup> e.g., formic acid, hydrofluoric acid, hydrochloric acid, solutions of the mineral acids (phosphoric and sulphuric acid) and also hydrogen sulphide.<sup>49</sup> Prepared in this manner, the viscous condensation product may be applied as an insulating lacquer to a metal surface. On exposure to formic acid vapor, the film loses its initially adhesive properties, forming a hard coating. Similarly, in the manufacture of molded lenses from transparent resin, the articles may be hardened at 60°C. until rigid enough to be removed from the mold without deformation. On exposure to hydrofluoric acid vapor for a day, or on dipping into 40 per cent hydrofluoric acid solution, the lens is stated to become hard enough for immediate polishing.

#### ELIMINATION OF FREE FORMALDEHYDE

The avoidance of any appreciable excess of free formaldehyde in the gelled polymerized mass is desirable, since its presence may lead to flaws and cracks during drying or during the molding process. Moreover, in the presence of much free formaldehyde the curing step seems to be retarded.<sup>50</sup> By adding substances which are capable of binding or decomposing free formaldehyde,<sup>51</sup> without forming gaseous bodies, the elimination of the excess of formaldehyde, and the transformation into clear, commercially practicable products is facilitated. Such substances are, notably, urea and thiourea, and also phenol. Alternatively, the formaldehyde may be destroyed by the addition of hydrogen peroxide.

The process may be carried out by making further additions of urea or thiourea to the gelatinous product of the initial condensation. Thus, 1 mol of urea is added for each 2 mols of free formaldehyde remaining after mixing 100 parts of urea with 600 parts of 40 per cent formalin and boiling until 60 per cent of the mixture has evaporated. The solution may then be concentrated at a temperature below 50°C. *in vacuo* until its viscosity has reached the highest value for which the operation of casting in molds is still practicable. The product, hardened at 60-100°C., is clear and does not become porous or clouded during molding due to liberation of formaldehyde. Moreover, the absence of gas evolution during curing at 100°C. aids the production of sharper moldings.

Pollak<sup>52</sup> described the preparation of transparent products free from uncombined aldehyde, in which urea is condensed with less than 2 mols of formaldehyde while

<sup>47</sup> M. Luther, W. Pungs, R. Griessbach and C. Heuck, U. S. P. 1,794,084, Feb. 24, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2253. R. Griessbach and M. von Blumencron, German P. 510,513, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1045. British P. 259,950, 1925; *Chem. Abs.*, 1927, 21, 3431.

<sup>48</sup> C. M. von Blumencron and E. Hochheim, German P. 511,970, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1346. British P. 264,466, 1926; *Brit. Chem. Abs. B*, 1928, 532.

<sup>49</sup> J. Lichtenberger, French P. 722,289, 1930, to Établ. Lambiotte Frères; *Chem. Abs.*, 1932, 26, 4191.

<sup>50</sup> British P. 291,266, 1927, to Kunstharzfabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1929, 23, 1227.

<sup>51</sup> F. Pollak and K. Ripper, U. S. P. 1,507,624, Sept. 9, 1924; *Chem. Abs.*, 1924, 18, 3458. F. Pollak, British P. 193,420, 1923; *Chem. Abs.*, 1923, 17, 3345.

<sup>52</sup> British P. 301,796, 1927, to Kunstharzfabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1929, 23, 4308. French P. 657,794, 1928; *Chem. Abs.*, 1929, 23, 4533. French P. 674,999, 1929, to Pollopa, Ltd.; *Chem. Abs.*, 1930, 24, 2846.

always maintaining some free formaldehyde in the reaction mixture, by the procedure of adding the urea gradually in progressively decreasing amounts. By a proper choice of the acid condensing agent, all the urea may be reacted before gelatinization occurs. A final acid polymerization may follow initial condensation in either neutral or alkaline solution.

Pollak<sup>53</sup> was of the opinion that restriction of the excess of formaldehyde present at any moment during the actual condensation did not permit of condensation being performed under optimum or even reproducible conditions. He thought the use of some excess was preferable, followed by removal of that excess, a step which may be performed either by reaction with further urea or thiourea or by the passage of a current of air or inert gas through the liquid at 80°C. Free, unreacted formaldehyde may thus be removed until its concentration has fallen to that value (usually 0.8-1.6%) which he considered necessary to avoid gelation of the resin.

Resins from urea and formaldehyde, said to be free from any deleterious products of side reactions,<sup>54</sup> may be obtained by mixing the condensation product of 1 mol of urea and less than 1.4 mols of formaldehyde with the product obtained by acid condensation of urea with more than 2 mols of formaldehyde, so that the ultimate ratio is about 1.8 mols of formaldehyde to 1 mol of urea. Thus, 60 parts of urea are dissolved in 347 parts of 30 per cent formaldehyde and boiled with 1 part of 10 per cent acetic acid. Then, 89 parts of urea are dissolved in 89 parts of 30 per cent formaldehyde, added to the first mixture during a period of 30 minutes and heated to complete the reaction.

Gams and Widmer,<sup>55</sup> in preparing resins free from excess formaldehyde, carry out the initial condensation in the presence of at least 2 mols of formaldehyde. Enough urea is then added that the mixture contains at least 1.05 mols of urea per mol of formaldehyde. A small proportion of an acidic compound is introduced at the same time. As an example, 320 parts of neutral 30 per cent formalin are refluxed with 120 parts of urea for 30 hours. After evaporation at a low temperature, 20 parts of urea and one-eighth part of sulphuric acid in 20 parts of water are added. No reaction occurs immediately. On evaporating the solvent water in a vacuum, there is formed a clear, viscous liquid, soluble in water, which hardens slowly on standing; the hardening takes place more rapidly on warming. The second portion of urea and the acid may alternatively be added at any stage during the concentration process. According to the final proportions of urea, the resins produced are transparent (with less than 1.1 mols of urea per 2 mols of formaldehyde) or translucent, becoming opaque with higher urea content. A stated advantage of this process is that the lowering of viscosity brought about by the second addition of urea enables dehydration to proceed much further before gelation occurs.

By incorporating a powdered reagent (urea or resorcinol) in a molding composition to fix liberated formaldehyde, glassy or porcellaneous products are obtained.<sup>56</sup> Sufficient urea may thus be added to bring the proportions down to 1.5 mols of formaldehyde per mol of urea. If desired, the secondary addition of urea may be made in such proportion that there still remains an excess of uncombined formaldehyde.<sup>57</sup> Free formaldehyde may be eliminated also by the addition of various sulphur compounds (hydrogen sulphide or ammonium sulphide).<sup>58</sup>

<sup>53</sup> F. Pollak, U. S. P. 1,950,746, Mar. 13, 1934, to Synthetic Plastics Co., Inc.; *Chem. Abs.*, 1934, 28, 3606.

<sup>54</sup> British P. 339,601, 1929, to Kunstharsfabr. F. Pollak G.m.b.H.; *Brit. Chem. Abs.* B, 1931, 262. French P. 680,110, 1929, to Pollopas, Ltd.; *Chem. Abs.*, 1930, 24, 3867.

<sup>55</sup> A. Gams and G. Widmer, U. S. P. 1,718,901, June 25, 1929, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1929, 23, 4031. British P. 249,101, 1926; *Brit. Chem. Abs.* B, 1927, 563. German P. 499,710, 1925; *Chem. Abs.*, 1930, 24, 4597. Canadian P. 281,327, 1928; *Chem. Abs.*, 1928, 22, 3270. See also British P. 413,489, 1933; *Brit. Chem. Abs.* B, 1934, 805.

<sup>56</sup> British P. 373,184, 1932, to Toledo Synthetic Products, Inc.; *Chem. Abs.*, 1933, 27, 3837. French P. 715,153 and 715,154, 1931; *Chem. Abs.*, 1932, 26, 1731.

<sup>57</sup> French P. 674,589, 1929, to Toledo Scale Mfg. Co.; *Chem. Abs.*, 1930, 24, 2906.

<sup>58</sup> J. Malet and R. Armenault, French P. 38,359, 1929, addn. to 679,321, to Fabr. de prod. de chim. de Laire; *Chem. Abs.*, 1932, 26, 1144.

According to Rothera, Blythen and Gillespie,<sup>50</sup> the use of at least two molecular proportions of formaldehyde is desirable in the preparation of initially clear, glass-like, resinous materials. Smidth,<sup>51</sup> however, observed that transparency in the ultraviolet region, also resistance to weathering, was favored by a high proportion of urea. If two mols of formaldehyde be condensed with one mol of urea, in a solution of  $p_H$  above 4, the dimethylolurea first formed undergoes further condensation with elimination of formaldehyde, which according to Smidth follows the approximate equation:



If, now, the liberation of formaldehyde be followed analytically, further adequate quantities of urea<sup>51</sup> may be added to react with it, maintaining the proportion of 1 mol of urea added for each 2 mols of free formaldehyde. The addition of urea is best carried out in such a manner that there is always a slight excess of free formaldehyde.

In this manner, up to 1.3 mols of urea may be condensed with 2 mols of formaldehyde. Thus, 50 cc. of 39 per cent formaldehyde ( $p_H = 5.0$ ) were refluxed with 19 g. of urea, and after 5 minutes of boiling, 15 drops of 1 *N* formic acid were added. On boiling .25 minutes longer, 3 g. more urea were added, and the whole boiled for an additional 5 minutes. The solution was then concentrated under reduced pressure during which operation the addition of a further quantity of urea could be made.

A related process, involving the addition of urea to the syrupy concentrate resulting from the evaporation *in vacuo* of the initial acid-condensed product, has been developed by Goldschmidt and Mayrhofer.<sup>52</sup> Cloudy, vitreous substances are thereby obtained which become transparent on standing or on treatment with acetic acid or acetone. By progressively adding 0.73-0.75 mol of urea to 2 mols of formaldehyde in the presence of acid condensing agents, clear resins may be obtained which are suggested as substitutes for plate glass.<sup>53</sup>

#### THE DEHYDRATION OF UREA-FORMALDEHYDE RESINS

The critical and important process of dehydrating the gelled resin condensation products may be performed, according to Ramstetter,<sup>54</sup> by addition of organic solvents, e.g., glycol chlorohydrin, glycol monoacetate, formamide, formic acid and acetic acid, during the condensation. When these solvents are distilled off, the water is completely removed also, leaving a clear anhydrous resin. Other substances, capable of forming volatile mixtures with water vapor and of giving transparent solutions of the condensation product, may be used, e.g., glacial acetic acid, benzyl alcohol or glycerol.<sup>55</sup>

The addition of the organic substance may be made either to the reaction mixture, or to the concentrated product. In producing lacquers, repeated addition and distilla-

<sup>50</sup> W. S. Rothera, S. Blythen and H. R. Gillespie, German P. 527,522, 1928; *Chem. Abs.*, 1931, 25, 5259.

<sup>51</sup> L. Smidth, U. S. P. 1,893,911, Jan. 10, 1933; *Chem. Abs.*, 1933, 27, 2280.

<sup>52</sup> Thiourea may be added in place of urea, according to L. Smidth (U. S. P. 1,704,347, Mar. 5, 1929, to E. G. Budd Mfg. Co.; *Chem. Abs.*, 1929, 23, 2000. U. S. Reissue 18,943, Sept. 12, 1933; *Chem. Abs.*, 1933, 27, 5907).

<sup>53</sup> S. Goldschmidt and R. Mayrhofer, German P. 551,422, 1927; *Chem. Abs.*, 1932, 26, 4425.

<sup>54</sup> S. Goldschmidt and R. Mayrhofer, German P. 561,050, 1928; *Chem. Abs.*, 1933, 27, 1113. F. Lauter (U. S. P. 1,671,596, May 29, 1928, to Rohm & Haas Co.; *Chem. Abs.*, 1928, 22, 2673) alleged that the cloudiness, apt to spoil transparent products, was due to the formation of methyleneurea.

<sup>55</sup> H. Ramstetter, German P. 403,645, 1922, to Badische Anilin- & Soda-Fabrik; *J.S.C.I.*, 1925, 44, 216B.

<sup>56</sup> K. Ripper, U. S. P. 1,762,456, June 10, 1930, to F. Pollak; *Chem. Abs.*, 1930, 24, 3867. U. S. Reissue 19,465, Feb. 12, 1935, to American Cyanamid Co.; *Chem. Abs.*, 1935, 29, 2264. See also F. Pollak, British P. 238,904, 1924; *Chem. Abs.*, 1926, 20, 2652. W. S. Rothera, S. Blythen and H. R. Gillespie, German P. 567,271, 1925; *Chem. Abs.*, 1933, 27, 1464.



tion of low-boiling solvents may be employed to remove water. In place of a single added substance, two different organic compounds may be used. The first may be a volatile constituent, e.g., amyl acetate, to carry off the water from the resin, and the other may be a less volatile or non-volatile substance (benzyl alcohol, glycerol or sugar) which is largely retained and modifies the properties of the resin. For instance, the addition of borneol or camphor gives rise to very flexible, highly plastic products. As an example, 150 parts of an intermediate condensation product are dissolved in 50 parts of alcohol, and 5 to 10 parts of benzene are added. A ternary mixture of water, benzene and alcohol is removed by vacuum distillation, and a repetition of the operation displaces the water completely, leaving an alcoholic solution of the resin to which 2 parts of borneol, dissolved in 50 parts of alcohol, are added. The solution obtained is evaporated to a syrupy consistency, and yields a resinous body which is hardened at 100°C.

The principle of forming constant-boiling mixtures with organic substances has been applied also by Crump.<sup>66</sup> Urea, dissolved in part of the formaldehyde, is added to the hot bulk of the formaldehyde, and the mass is concentrated *in vacuo* while still in the soluble form. An organic liquid (e.g., butyl alcohol) is added and removed by boiling in an open pan. In this way water is very completely removed as a constant-boiling mixture.

Aqueous dispersions of urea-formaldehyde resins containing dyes, plasticizers or modifying agents may be dehydrated by spraying into a stream of gas heated to a temperature higher than the boiling point of water for the prevailing pressure.<sup>67</sup> Gases suggested for the purpose are air, carbon dioxide, helium or vapors of diphenyl oxide.

The addition of non-volatile substances miscible both with the urea-formaldehyde colloid and with water<sup>68</sup> (e.g., glycol), before concentration of the solution of the condensation product, also assists in the elimination of water. Cherry<sup>69</sup> reported that the addition of sucrose (20 per cent of the amount of urea used) enabled clear molded articles to be made without cracking.<sup>70</sup> Dearing<sup>71</sup> stated that gum acacia was analogous to sucrose in its action with urea condensates.

If the product is dehydrated by merely evaporating off the water, measurements of the specific electrical resistance (or conductivity) of the reaction mixture serve as indications of the rate of evaporation.<sup>72</sup> A mode of control is obtained by this means, and interruption of the process at a particular point is made possible.

Solvents may be removed from liquid urea-formaldehyde condensates by subjecting the dispersion to steam distillation, according to Pungs, Eisenmann and Kuchenbuch.<sup>73</sup> A hydrophobe gel is thereby obtained, from which much water may be removed by kneading or rolling. By rolling into thin strips, the substance may be dried more easily and thoroughly, becoming clear and glass-hard. The pulverized product may be first dried *in vacuo*, which gives a solvent-free material that can be molded. These investigators also extracted the solid condensation products with volatile non-hydroxylic solvents, e.g., ether, benzene or methyl formate, separating the resin into two fractions. One fraction is an insoluble, glass-like solid, the other, making up 15-20 per cent of the whole, is a colorless, viscous gum, which may be used as a softening agent for cellulose derivatives, or as

<sup>66</sup> J. W. Crump, British P. 309,849, 1928, to Bakelite, Ltd.; *Chem. Abs.*, 1930, 24, 740. French P. 658,411, 1928; *Chem. Abs.*, 1929, 23, 5339.

<sup>67</sup> British P. 408,689, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 5693.

<sup>68</sup> French P. 736,744, 1931, to Soc. Nobel française; *Chem. Abs.*, 1933, 27, 1531.

<sup>69</sup> O. A. Cherry, U. S. P. 1,799,954, Apr. 7, 1931, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1931, 25, 3136.

<sup>70</sup> Resins prepared with sugars, formaldehyde and urea are discussed in Chapter 36.

<sup>71</sup> M. C. Dearing, U. S. P. 1,982,795, Dec. 4, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 525.

<sup>72</sup> R. Griessbach and C. Müller, German P. 487,013, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1189.

<sup>73</sup> W. Pungs, K. Eisenmann and J. Kuchenbuch, U. S. P. 1,889,791, Dec. 6, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1774. German P. 519,893, 1929; *Chem. Abs.*, 1931, 25, 8448. British P. 332,634, 1929; *Chem. Abs.*, 1931, 25, 389. French P. 688,185, 1930; *Chem. Abs.*, 1931, 25, 835.

an adhesive. The solid fraction, like the original condensation product, is soluble in polyhydroxy compounds, higher ketones (e.g., cyclohexanone), furfural and ethers such as dioxane.

Feinmann<sup>74</sup> also fractionated urea-formaldehyde resins into portions with differing properties. The hot resin is treated with just sufficient water to cause separation into two layers after cooling to 15°C. The upper, aqueous layer is separated, and more water added to it to precipitate the condensation product. A separation is thus achieved of the insoluble and partially water-soluble fractions of the resin.

### ORGANIC GLASS

The various types of "organic glass" manufactured from urea-formaldehyde resins usually possess a transparency to ultraviolet light superior to that of ordinary

#### ULTRAVIOLET TRANSMISSION OF VARIOUS GLASSES

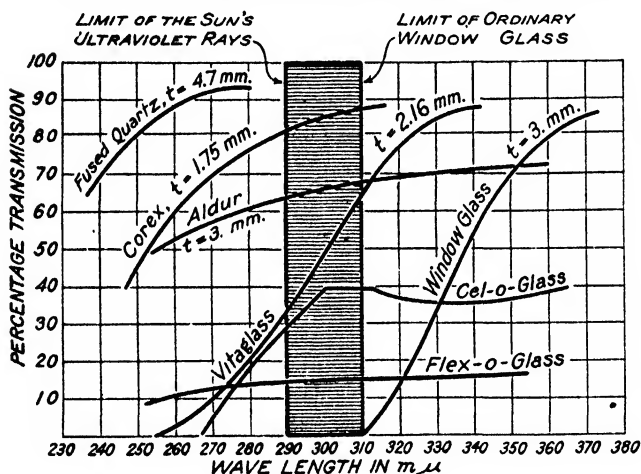


Fig. 92.

Comparison of the Ultraviolet Transmissibility of Various Glasses. (R. H. Crist)

Courtesy Industrial and Engineering Chemistry

window glass.<sup>75</sup> This fact, together with the resistance of the resins to discoloration on exposure to light, suggests their introduction as substitutes for ordinary glass. The observation that urea and formaldehyde would unite to form, on drying, a glass-like solid was formerly considered a discovery of the greatest importance. The announcement of this work was published in various journals discussing popular science and has led to much misapprehension. The statement has appeared that the clear material made in this way resembles glass in transparency but is much tougher and more serviceable in applications where the fragility of glass comes into question. These statements have not been borne out in actual practice.

In the first place the surface of the urea resin "glass" is soft relative to glass itself and is easily scratched. Likewise, because of its lack of adequate water-resistance, the surface becomes dulled on long exposure to humid conditions. The reaction between urea and formaldehyde, moreover, is not complete at the time

<sup>74</sup> I. Feinmann, British P. 397,909, 1932; Brit. Chem. Abs. B, 1933, 929. French P. 752,431, 1933; Chem. Abs., 1934, 28, 1293.

<sup>75</sup> For a short discussion of the light-transmitting characteristics of organic plastics, see Chem. Met. Eng., 1933, 40, 469.

the "glass" is prepared and the subsequent progress of the reaction tends to set up stresses and strains in the sheet or article made from the resin, resulting eventually in the spontaneous formation of cracks and fissures. Oftentimes these do not appear for a long period after the product has been made, but in due course they occur and the article made from the urea resin stock becomes disfigured and worthless.

One type of urea-formaldehyde resin<sup>76</sup> that has been developed in an attempt to find a substitute for glass is, when freshly prepared, transparent to both visible and ultraviolet light and has a specific gravity of 1.44. The refractive index of the product varies from 1.6-1.9, and the hardness is 2.95 on Moh's scale (the hardness of glass is 4.5-6.5). Its light-dispersive properties are similar to those of quartz crystal, which has suggested application to the production of optical parts. The material can be turned and does not melt on heating but chars at about 200°C.<sup>77</sup>

Crist<sup>78</sup> has made a study of the ultraviolet transmission of a proposed glass substitute consisting of a condensation product of formaldehyde and urea. The percentage transmission at different wave lengths is given in Table 32, and a comparison with other glasses is shown in Figure 92 taken from the work of Crist and that of Coblenz and Stair.<sup>79</sup> The sample used was clear, 3 mm. thick and had polished surfaces.

TABLE 32.—Transmission of Window-glass Substitute

Wave Length Å	Per Cent
2540	48
2700	56
3130	68
3650	74
4360	80
6150	93

Kostka<sup>80</sup> observed that urea-formaldehyde resins show a readily distinguishable faint fluorescence when irradiated with ultraviolet light. However, phenol-formaldehyde resins, which absorb ultraviolet radiation, do not fluoresce. The ultraviolet opacity of the phenol resins affords a ready means of distinguishing them from urea-formaldehyde products. Katowaki and Kasai<sup>81</sup> found that urea-formaldehyde resin transmits rays having a wave length as short as 2300Å. A thio-urea-formaldehyde resin, cured at 55°C., is said to have the next best transparency. Both resins darkened on exposure to light of long wave length because of the presence of water in the resin. A methylurea-formaldehyde resin had a range of transparency similar to that of ordinary glass, whereas a product prepared from ethylurea completely absorbed all light in the ultraviolet region.

<sup>76</sup> This product, known as "Pollopos," was based on the work of F. Pollak of Vienna. It was sold in the United States as "Luxite" (*Plastics* 1929, 5, 350). See also C. Marx, *Plastics*, 1925, 1, 85. F. Pollak and K. Ripper, *Chem. Ztg.*, 1924, 48, 569, 582. H. R. Schulz, R. Schmidt and I. Schmidt, *Keram. Rundschau*, 1925, 33, 143; *Chem. Abs.*, 1926, 20, 1502. *Plastics*, 1927, 3, 400. *Ind. Eng. Chem., News Ed.*, 1927, 5, 15. *Oil, Paint and Drug Rep.*, 1926, 109(9), 21; *Chem. Abs.*, 1926, 20, 1891. A similar urea-formaldehyde product, "Prystal," has also been developed in an endeavor to produce a glass-substitute (H. Barthélemy, *Chim. et ind.*, 1926, 16, 367; *Brit. Chem. Abs. B*, 1926, 955. *Cf. Plastics*, 1927, 3, 324).

<sup>77</sup> W. Landgraeber, *Asphalt Teerind. Ztg.*, 1926, 26, 1042; *Chem. Abs.*, 1927, 21, 2172. See also *Molded Products*, 1927, 3, 372, 504; *Plastics*, 1927, 3, 214.

<sup>78</sup> R. H. Crist, *Ind. Eng. Chem.*, 1928, 20, 1367. The product studied was "Aldur" (See N. Klein, *Plastics*, 1928, 4, 588). Aldur was made by the Lucio Products Corp.

<sup>79</sup> W. W. Coblenz and R. Stair, *Trans. Illum. Eng. Soc.*, 1928, 23, 247, 1121; *Chem. Abs.*, 1929, 23, 944.

<sup>80</sup> G. Kostka, *Chem. Ztg.*, 1929, 53, 117; *Brit. Chem. Abs. B*, 1929, 293.

<sup>81</sup> H. Katowaki and Y. Kasai, *Repts. Imp. Ind. Research Inst., Osaka, Japan*, 1932, 13(3), 25; *Chem. Abs.*, 1933, 27, 1719.

Gams and Widmer<sup>82</sup> employed sheets of urea-formaldehyde resin (without any glass) in constructing a laminated material designed to replace glass in wind-shields and other products. For this purpose it is proposed to use the resin in two distinct stages of condensation, the less-condensed substance serving as an adhesive for sheets of the more highly polymerized material.

To obtain the more highly condensed resin, 5 kilos of urea are dissolved in 12.7 liters of 40 per cent formaldehyde, and the solution is filtered after the addition of 600 g. of animal charcoal. The filtrate is heated for 8 hours at 100°C. in an autoclave and evaporated at a low temperature. After adding 100 g. of phosphoric acid, the resin is cast in molds and hardened by increased temperature. The softer resin is prepared similarly, but together with the phosphoric acid is added 500 g. of benzyl alcohol as a softening agent. When the resins have been hardened into a workable glassy mass, thin sheets are cut, and a sheet of the soft resin is laid between two sheets of the hard resin. This combination of layers is then pressed for an hour at 100°C. and 50 atmospheres pressure. The resulting plate is further hardened by the usual methods until the polymerization of the resin is complete.

Capart<sup>83</sup> suggested that the strength and mechanical properties of glass-like urea resins could be improved by surfacing them with colloidal deposits of metals or metalloids. The metallic covering may be used, according to this investigator, as a conducting medium for the electrodeposition of other metal layers in the production of mirrors. Walter<sup>84</sup> hardened the surface of organic glasses by applying a harder, transparent varnish (e.g., a cellulose lacquer) as a coating.

When urea-formaldehyde condensation products are formed in water solution at a controlled hydrogen ion concentration, followed by evaporation of the solvent, drying and aging, strain is liable to develop and may cause cracking or disintegration of the molded product as has already been indicated. Smidth and Crist<sup>85</sup> heated a cast urea resin (prepared from 1.2 mols of urea and 2 mols of formaldehyde) in a bath of mineral oil at about 165°C. At this temperature the resin softens. The softening step is said to relieve strains causing possible deterioration, and at the same time the article can be shaped while in the plastic condition. The heating time is generally 1 minute.

Müller<sup>86</sup> formed transparent, glass-like materials by molding urea-formaldehyde condensation products in closed molds made of non-metallic substances (e.g., glass and plywood) and dried the molded articles in a moist medium until the specific gravity no longer varied. Before completion of the drying, the molded piece was compressed. Specifically, 80 kg. of paraformaldehyde, 50 kg. of water and 63 kg. of urea are heated with 4 liters of 2 *N* sodium hydroxide, until dissolved, and then refluxed for 1 hour. A condensation product (10 kg.) of glycerol and adipic acid is added, and the refluxing is continued. Then 6 kg. of 2 *N* sulphuric acid, in which 2 kg. of urea are dissolved, are introduced into the mixture, and the whole is boiled until clear. The resulting liquid is cooled in the prepared molds and removed after 6-8 hours as a homogeneous, transparent, molded article ready for the drying process. The drying is accomplished by treating the product with air of progressively rising temperature and diminishing humidity. During the air-drying, the article is rested on a support having a shape similar to that of the original mold.

<sup>82</sup> A. Gams and G. Widmer, U. S. P. 1,802,246, Apr. 21, 1931, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1931, 25, 3448. British P. 286,250, 1927; *Brit. Chem. Abs. B*, 1928, 792. French P. 737,654, 1932; *Chem. Abs.*, 1933, 27, 1724. French P. 649,602, 1928; *Chem. Abs.*, 1929, 23, 3062.

<sup>83</sup> G. P. Capart, French P. 683,033, 1929; *Chem. Abs.*, 1930, 24, 4004.

<sup>84</sup> G. Walter, French P. 735,075, 1931; *Chem. Abs.*, 1933, 27, 1118.

<sup>85</sup> L. Smidth and R. H. Crist, U. S. P. 1,886,600, Nov. 8, 1932, to Luco Products Corp.; *Chem. Abs.*, 1933, 27, 1404.

<sup>86</sup> T. Müller, French P. 755,331, 1933; *Chem. Abs.*, 1934, 28, 1559. British P. 408,460, 1934; *Chem. Abs.*, 1934, 28, 6004. British P. 419,306, 1933; *Brit. Chem. Abs. B*, 1935, 69.

Urea plastics were used by Ramstetter<sup>87</sup> for making lenses and optical parts. Reference also may be made here to a method of manufacturing large disks from urea-formaldehyde resins.<sup>88</sup> The principal features of the method include the use of large, closed vertical molds made of acid glass and the drying of the molded disks in an air stream of gradually rising temperature and a humidity 10-40 per cent below the saturation pressure of water vapor at the prevailing temperatures.

<sup>87</sup> H. Ramstetter, German P. 416,753, 1923, to Badische Anilin- & Soda-Fabr.; *Brit. Chem. Abs. B*, 1926, 203.

<sup>88</sup> A. Müller, E. Gerisch and W. Beuschel, German P. 584,398, 1933, to Ambi-Verwaltung A.-G.; *Chem. Abs.*, 1934, 28, 352. German P. 596,618, 1934; *Chem. Abs.*, 1934, 28, 5264.

## Chapter 28

### Urea Resins

#### II. Hot-Molding Compositions. Fillers

The conditions for making a satisfactory molded product in which urea resin<sup>1</sup> forms the binding agent or plastic material are very complicated. For one thing it has been found useful in reacting urea and formaldehyde to maintain a definite pH control<sup>2</sup> because the degree of acidity or alkalinity of the composition materially influences the flow or plasticity of the molding composition. It is also necessary to have a composition available which on molding shrinks very slightly in the mold and gives sufficient opportunity to remove the finished article easily. At the same time, shrinkage must not be great enough to exceed the tolerance limits for the dimensions of the molded piece.

Another point which should be noted in connection with products of the kind under discussion is that a molded article from a urea resin tends to absorb moisture in humid weather and to give it out in a dry atmosphere. Thus there progresses a constant, very slight expansion due to moisture take-up and a corresponding shrinkage when such absorbed water is removed by drying. This change, however, is so slight that it does not result in fracture of the molded article.

Due to this attraction for moisture, molded articles from urea resins are not absolutely water-resistant, and the degree of resistance depends in a large measure on the method of making the molding composition as well as on the degree of cure. It is customary in testing the molded articles to boil a specimen in water for a given time, remove, dry and note the character of the surface. At the same time weighings are frequently made to determine the amount of water-absorption under the conditions of this test. Should the molded specimen, after drying, present a smooth, glossy surface, it is usually considered satisfactory but, on the other hand, if blisters have formed or disintegration has set in with deformation of the article, the product is not acceptable for most purposes.

One important advantage which the urea resin molding compositions possess over those of the phenol-formaldehyde type is the relative translucency of the molded goods. It is possible to add colors to a refined phenol-formaldehyde resin and obtain very good shades, especially with the darker pigments, but articles molded from compositions so pigmented are decidedly opaque, lacking the slight measure of transparency or translucency of surface which gives to the molded articles from urea resin a brilliancy and depth of color that is not easily obtained by any other thermosetting composition.

<sup>1</sup> For reviews concerning the use of urea-formaldehyde products in the molding field, see: Carleton Ellis, *Chem. Met. Eng.*, 1928, 35, 18; *Ind. Eng. Chem.*, 1934, 26, 38. J. Scheiber, *Farbe u. Lack.*, 1931, 170; *Chem. Abs.*, 1931, 25, 3501. F. Schmidt, *Kolloid-Z.*, 1923, 46, 324; *Brit. Chem. Abs. B*, 1929, 125. W. C. Hirsch, *Elec. Mfg.*, 1931, 7, 49. A. A. Drummond, *Chem. Age (London)*, 1928, 19, 624. H. V. Potter, *J.S.C.I.*, 1922, 51, 869. See also *Chem. Met. Eng.*, 1929, 36, 569; 1933, 40, 42.

<sup>2</sup> See M. Dérivière, *Rev. gén. mat. plastiques*, 1933, 9, 466; *Chem. Abs.*, 1934, 28, 3191. See also Chapter 27.

Molding compositions containing urea resins can be processed to yield articles which are white, ivory or cream colored, and by the addition of pigments the pressed articles may be given a variety of the lighter tinted shades which are particularly desired.

Much study has been devoted to the problem of obtaining colors or pigments for the urea resin compositions which will give molded articles that are fast to light while still possessing light tones or pastel shades. In the manufacture of molding compositions difficulty arises in matching colors. A product may be made of a given shade and sold and then, when the consumer of the molding composition wishes to duplicate his order, the factory has to produce the same shade. This may be of a delicate cast and difficult to reproduce, hence the plants producing the molding compositions have on hand men who are experts in color matching.

The earlier products placed on the market were prepared by reaction between formaldehyde and mixtures of urea and thiourea. These substances react with formaldehyde in the same manner, that is, they yield methylol derivatives which condense to resins, but although equivalent in a generic sense the urea resins are displacing those from thiourea or from mixtures of urea and thiourea. The latter gives strength to the molded article but retards the rate of cure, with the result that the resins containing thiourea are not particularly in favor with a molder who seeks to obtain from his presses a large daily production. A further disadvantage arises in the action of thiourea on the steel molds used in molding establishments. Sulphur present in the thiourea blackens an ordinary steel mold and in the course of time the surface of the mold is impaired and consequently the molded articles do not possess the desired surface finish. To offset this, stainless steel or chromium-plated molds have been used, but the cost of molds, even when made from cheaper grades of steel, is so high that any additional cost of mold making is frowned upon by the molders who require such equipment. The plating on molds protected in this manner is worn off in the course of time, especially at projecting parts of the mold walls where the flow of the composition is particularly severe and renewal of the plating is then needed. In view of these disadvantages the use of thiourea with urea is comparatively limited, although in some cases where a particular degree of strength and high water-resistance is required a portion of the urea may be replaced by thiourea.

The specifications of the molder with respect to flow of the material, surface finish and particularly absence of blistering are extremely precise and the manufacturer of urea resin molding compositions has to conduct his manufacture in the most exact manner with every possible method of control in hand in order to meet these requirements (see Figure 93). If a molding composition during hot pressing generates gases too easily the molded article will show blisters either on the surface or in the interior, which of course cause distortion and defacement. It is sometimes customary, in molding plants where urea resin molding compositions are used, to relieve the mold of gases by raising the platen during the earlier stages of cure. If a very rapid molding composition is being used, it is generally sufficient simply to apply pressure, then immediately relieve the pressure and after the escape of gas, which occurs quickly, the press is closed until the cure is effected.

As urea resin molding compositions are desired particularly to provide molded articles which are white, ivory-colored or of various delicate shades of color, the problem arises of avoiding the introduction of dirt and dust into the molding composition and also of molding under conditions which preclude the inclusion

of foreign matter. In the resin factory it is possible to filter the air entering the plant and to conduct the manufacturing operations with due regard for cleanliness in an effort to prevent the entrance of foreign particles. The molders, however, are not so well situated, since their plants as a rule are operating on phenol-formaldehyde products, which are generally dark in color. Therefore there is much dust in such molding establishments which is liable to get into the light-colored molded urea resin pieces and cause stains and specks. The defacement which results thus may cause a considerable number of rejections. Further, it should be noted that molds which have been used for phenol-formaldehyde products generally are difficult to clean adequately for use in molding light-colored urea resin articles. For this reason it is recommended that the molder avoid make-



*Courtesy Monsanto Chemical Co.*

FIG. 93.—Compression Molding Press from which a Resin-Impregnated Pre-form Is Being Removed.

shifts and have a building or department for molding urea resins entirely separate from the phenol-formaldehyde work and to use every possible care to keep the urea-formaldehyde section free from dust. In the past a number of complaints which have arisen because of rejection of urea moldings have been blamed on the manufacturer by the molder, when in reality the molder himself may be responsible due to operation in an inappropriate, dusty environment.

#### ACID CONDENSING AGENTS

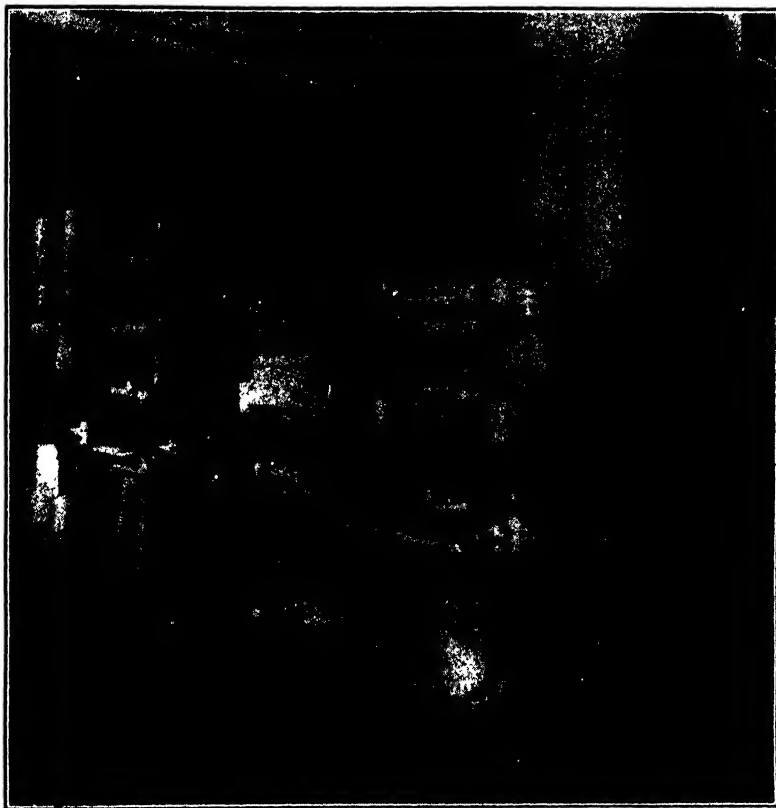
It was found by Ellis<sup>3</sup> that the wide range of temperature between the hardening points of the methylolureas and their decomposition temperatures renders them especially suited to the manufacture of firm, heat-resistant, molded articles. Thus, dry dimethylolurea gave a white material which could be molded at 150°C. under 1000 lb. pressure. The glossy molded product carbonized and burned, without melting, when held in the flame of a Bunsen burner. Resins of this type also may be incorporated in phenol-formaldehyde or phenol-furfural resins, making modified molding compositions. Aniline-furfural resins, phenol-sulphur resins or

<sup>3</sup> Carleton Ellis, U. S. P. 1,536,881, May 5, 1925; *Chem. Abs.*, 1925, 19, 1956.



natural gums (cracked Congo resin) are also capable of incorporation with methylolurea.

In the preparation of molding compositions, the acid used to bring about polymerization of the urea condensation product is, to some extent, retained by and catalyzes the hardening of the resin. Hence, those acids having no deleterious action on the mold are desirable. Thus,<sup>4</sup> dimethylolurea may be "polymerized" by



*Courtesy Hydraulic Press Mfg. Co.*

FIG. 94.—Battery of Small Hydraulic Presses.

phthalic anhydride or oxalic acid. By keeping the composition slightly acid, the material is less likely to be discolored on heating than if alkalis are present.

The nature of the acid condensing agent used may have some effect on the properties of the resins formed.<sup>5</sup> If 20 parts of urea be mixed with 54 parts of 40 per cent formaldehyde, in the presence of 0.4 part of caustic alkali, condensation may be checked at the stage of dimethylolurea by neutralization with acetic acid or phthalic acid as soon as a turbidity appears. The resulting solution, which is stable indefinitely, may be coagulated (e.g., in a mold) by the addition of a small quantity of strong acid. Modifying agents such as casein, gelatin, dyes or fillers are added. The castings are allowed to stand until hard enough to handle,

<sup>4</sup> Carleton Ellis, U. S. P. 1,536,882, May 5, 1925; *Chem. Abs.*, 1925, 19, 1956.

<sup>5</sup> Carleton Ellis, U. S. P. 1,846,853, Feb. 23, 1932; *Chem. Abs.*, 1932, 26, 2609

then dried superficially in the air. The material can be machined, and if water is expelled by heating, the product becomes transparent and hard. The mineral acids or acid salts used for coagulating may, however, be replaced by organic acids. For example, when urea, phthalic anhydride and aqueous formaldehyde are heated together they form a thin, transparent syrup which becomes heavy-bodied on cooling. This may be diluted with alcoholic or ketonic solvents (e.g., with an equal bulk of acetone) to form varnishes or impregnating media that yield transparent coatings when baked. The condensation product embodying phthalic anhydride is more resistant towards discoloration by heat than the unmodified urea-formaldehyde resins.

A resin of this type is made by boiling 15 parts of urea with 15 parts of phthalic anhydride and 60 parts of 40 per cent formaldehyde, then drying at 50°C. until the material can be cut into strips or sheets, which on air-drying give a clear, glassy material that is suggested as a substitute for glass for some purposes. By baking at 110-130°C., the material is rapidly made insoluble and can be used as a molding composition. Employed in this manner, with asbestos, wood flour or other filler, molded articles leave the mold freely, no mold-lubricant being necessary. In compositions of this type, phthalic acid is replaceable by other acids, e.g., benzoic acid, citric acid, gallic acid and trichloroacetic acid, giving rise to a considerable variation in the toughness, color and other properties of the products.

A study of these various acid condensing-reagents was made by Ellis\* who found that although mineral acids scarcely enter into combination with the urea-formaldehyde products, organic acids have a greater tendency to form resinous complexes. In the following succinct account of the experimental findings, 1 part of the designated acid is boiled with 1 part of urea and 4 parts of a 40 per cent formaldehyde solution:

(1) Benzoic acid gives a white, opaque, syrupy liquid containing much crystalline material, after boiling for 5 minutes. This substance hardens readily to a fairly white product when heated on a hot plate.

(2) With citric acid the mixture effervesces on heating, giving a clear syrup. On a hot plate, the material rapidly hardens with slight yellowing.

(3) The reaction is exothermic with acetic anhydride and a clear, white jelly is obtained. A snow-white, infusible, glossy mass results on the hot plate.

(4) Propionic acid gives a mild reaction leading to a white, non-syrupy solution. A transparent, hard, white mass is obtained by heating on a hot plate.

(5) On heating the ingredients with gallic acid, a clear, thick, syrupy solution forms, which becomes clouded and slightly yellowish on heating. Hot-plate treatment gives a hard, glossy, yellowish resin.

(6) Lactic acid gives a clear, syrupy solution which hardens to a yellowish resin on the hot plate.

(7) Boiling the ingredients with maleic acid yields a slightly yellow, thin syrup (free from sediment) which gives a spongy, brownish, rather weak mass on the hot plate.

(8) Treatment with salicylic acid results in the formation of a water-white syrup with some white, crystalline residue. If this is heated on the hot plate a tough, snow-white resin forms readily.

(9) When tartaric acid is heated with the mix, effervescence is observed and a clear, not particularly syrupy solution results. Heating on the hot plate gives a fairly tough, pure white resin.

(10) Acetyl salicylic acid forms a thick syrup, transformable into a transparent jelly. This reacts very quickly on the hot plate to produce a transparent resin.

(11) With oxalic acid, a clear, rather thin, light-colored syrup is obtained which on heating (hot plate) sets to a hard mass.

(12) A white syrup with much white solid matter resulted on reacting the materials with mucic acid. Hot-plate treatment converts the product to a white resin, tougher than that obtained with maleic acid.

(13) By using tannic acid, a yellow solution passing through a syrupy stage to a

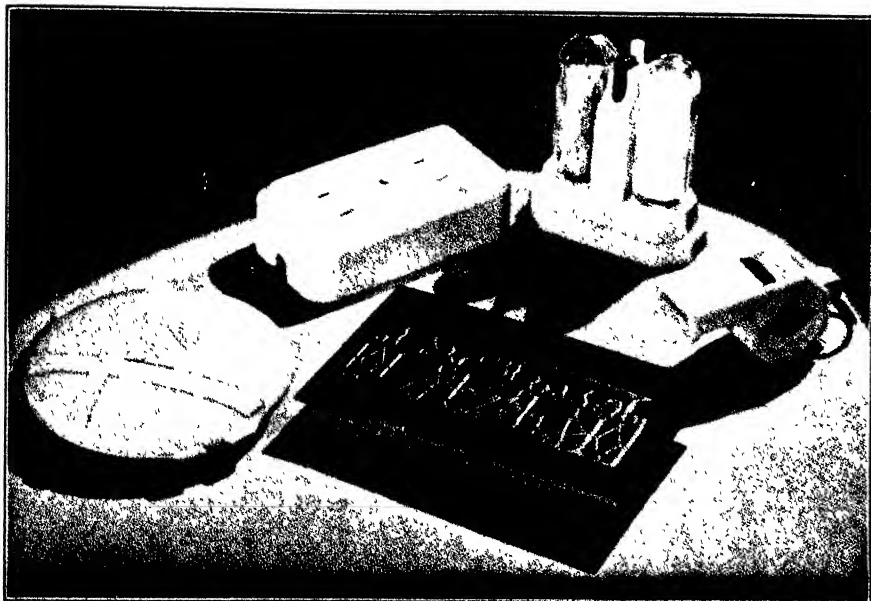
\* Carleton Ellis, *loc. cit.*

thin, transparent, yellowish brown jelly is obtained. After a brief hot-plate curing, a dark brown resin remains.

(14) A vigorous, jelly-forming reaction occurs with trichloroacetic acid. Further curing gives a white resin possessing considerable elasticity

(15) Stearic acid gives a poor reaction with much separation. The product obtained on the hot plate is opaque and lacks strength.

According to Luther and Haag,<sup>7</sup> water-soluble, crystalline products are obtained by the condensation of at least 2 mols of urea with 1 mol of formaldehyde by means of acid condensing agents in organic solvents (e.g., ethyl acetate). In water, condensation proceeds further, forming substances differing from methylencurea in that they are soluble in hot water. Having a lower solubility than



Courtesy Unyte Corporation

Fig. 95.—Molded Articles of Unyte. The inlay piece shown consists of stamped metal, chromium-plated, molded into a sheet of Unyte.\*

\* Compact manufactured by American Record Corporation.

urea and a high nitrogen content, these bodies have been suggested for use as fertilizers and fungicides.

In the preparation of resins containing less than 2 mols of formaldehyde per mol of urea, condensation products very low in retained water are obtained by adding to the reaction mixture buffer compounds which, at the same time, reduce swelling.<sup>8</sup> The substances used for this purpose are the polybasic organic acids (citric acid), their salts and the salts of aluminum and other polyvalent metals with organic acids.<sup>9</sup> These are employed as the sole buffering agents.

Salts and other compounds undergoing acid hydrolysis are also used.<sup>10</sup> Such

<sup>7</sup> M. Luther and W. Haag, German P. 528,582, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 5259.

<sup>8</sup> M. Luther, W. Pungs, R. Griessbach and C. Heuck, U. S. P. 1,952,593, Mar. 27, 1934; to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3540.

<sup>9</sup> Titanium citrate, lactate or tartrate may be used in the resin-forming reaction (French P. 763,066, 1934, to Soc. Ind. des vernis adhésifs; *Chem. Abs.*, 1934, 28, 5263).

<sup>10</sup> M. Luther and C. Heuck, U. S. P. 1,791,062, Feb. 3, 1931, to I. G. Farbenind. A.-G.; *Chem.*

substances are magnesium chloride, formamide and formic ester. Thus, 1200 parts of urea in 800 parts of water are condensed with 4000 parts of 30 per cent formaldehyde in the presence of a sodium acetate-acetic acid buffer. After condensation, 7 parts of dilute sodium acetate solution are added, and the mixture concentrated *in vacuo*. Before completion of the evaporation step, a concentrated solution of 10 parts of magnesium chloride is added. The viscous product is completely hardened by keeping at 70°C. for 12 hours.

#### $p_H$ CONTROL

Ellis<sup>11</sup> observes that, between the  $p_H$  limits 4-8 customarily used for the initial stage of condensation, the time required for reaction varies with the hydrogen-ion concentration. At the same time, the  $p_H$  of the mixture changes slightly during reaction, e.g., from 6 to 5.1. The time required for drying the resin is also related to the period of heating during condensation. If the latter operation be advanced as far as possible in the liquid phase without gelation, the drying is expedited and may be carried out in air or in a vacuum drier, below 50°C. Avoidance of pre-curing during drying is essential if the molding properties of the resin are to remain unimpaired.

Cherry<sup>12</sup> recommended that the condensation of urea and formaldehyde be carried out at a  $p_H$  of 5. This value is attained in commercial formaldehyde solutions (containing usually 0.02-0.03 per cent of formic acid) in the presence of lead, manganese or other heavy metal acetates as buffering salts. In the presence of a reactive metal (zinc), the formic acid reacts to yield zinc formate, which exercises a buffering action. According to another procedure,<sup>13</sup> condensation may be carried out at a  $p_H$  of 3, and the  $p_H$  of the solution raised to 7 before it is concentrated. The final reaction of the concentrated product may then be effected by acidifying so that the  $p_H$  is between 3 and 5. Goldschmidt and Gerische<sup>14</sup> prepared condensation products by refluxing paraformaldehyde, urea and a small amount of 2 *N* sodium hydroxide. Sulphuric acid was then added and heating continued until a viscous mass was formed. After adding ethyl alcohol (or other lower alcohol), the mixture was cooled. The product remained fluid for several days and then gelatinized. A modification of this reaction entails the use of trioxymethylene, butyl alcohol, urea, 0.5 *N* sodium hydroxide and 0.5 *N* sulphuric acid.<sup>15</sup> The method employs super-atmospheric pressures by performing the reaction in an autoclave heated to 135°C.

The formaldehyde used in urea-aldehyde condensations can be treated with magnesium carbonate to control the  $p_H$  of the reaction mixture. Thus, Ellis<sup>16</sup> added 10 parts of light magnesium carbonate (this may be prepared from cold dilute solutions of magnesium sulphate and sodium carbonate) to a mixture containing 840 parts of urea, 300 parts of thiourea and 2250 parts of formalin. The initial  $p_H$  of 7 changed to 8.4 on heating over a period of 10-12 minutes up to 65°C., and at the temperature

*Abs.*, 1931, 25, 1645. German P. 535,852, 1925; *Chem. Abs.*, 1932, 26, 1404. British P. 278,698, 1926; *Chem. Abs.*, 1928, 22, 2645. French P. 643,104, 1927; *Chem. Abs.*, 1929, 23, 1482. See also German P. 537,611, 1926; *Chem. Abs.*, 1932, 26, 1404. German P. 542,785, 1926; *Chem. Abs.*, 1932, 26, 3344. German P. 557,427, 1925; *Chem. Abs.*, 1933, 27, 817.

<sup>11</sup> Carleton Ellis, U. S. P. 1,905,999, Apr. 25, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 3629.

<sup>12</sup> O. A. Cherry, U. S. P. 1,737,918, Dec. 3, 1929, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1930, 24, 930.

<sup>13</sup> O. A. Cherry, U. S. P. 1,790,461, Jan. 27, 1931, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1931, 25, 1346. E. C. C. Baly and E. J. Baly (British P. 301,626, 1927, to Pollopos, Ltd.; *Chem. Abs.*, 1929, 23, 4308) recommend an aqueous solution with a  $p_H$  of 5-7 for the condensation.

<sup>14</sup> S. Goldschmidt and E. Gerische, German P. 584,856, 1933, to Ambi Verwaltung A.-G.; *Chem. Abs.*, 1934, 28, 1154.

<sup>15</sup> W. Fungs and K. Eisenmann, U. S. P. 1,967,685, July 24, 1934, to Unyte Corp.; *Chem. Abs.*, 1934, 28, 5941.

<sup>16</sup> Carleton Ellis, U. S. P. 1,905,999, Apr. 25, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 3629.

of boiling the  $p_H$  was 7.8. According to Dearing,<sup>17</sup> a stable formaldehyde solution with a  $p_H$  of 7.1 can be obtained by adding 2.5 per cent (by weight) of basic magnesium carbonate to commercial formalin. This solution maintains its neutrality over long periods of time.

Two or possibly three factors influence the production of water-soluble urea-formaldehyde condensates; these are (1) the  $p_H$  of the condensing medium, (2) the ratio of urea to formaldehyde, and (3) in some cases on the rate of addition of the urea to the formaldehyde. By reacting 1 mol of urea with 2 mols of formaldehyde in a medium having a  $p_H$  of 5, Dearing<sup>18</sup> obtained a condensate which gave a water-insoluble precipitate upon dilution with a large amount of water after the elimination of free formaldehyde. The product, which may be molded with heat and pressure, is at first fibrous, but becomes amorphous after washing with fresh quantities of water.

Dearing<sup>19</sup> prepared a molding powder by employing an initial  $p_H$  of 5 and adding acid to complete the condensation. Thus, 800 parts of water and 60 parts of urea are added to 300 parts of formalin (adjusted to a  $p_H$  of 5). The solution is boiled for one minute, and 30 parts of urea are introduced. After an additional one minute interval 21 parts of urea are added; and the refluxing is continued for one hour, adding 2 parts of hydrochloric acid (sp.gr. 1.18) at the end of this period. The solution is boiled five hours longer with the subsequent addition of 5 parts of hydrochloric acid. While the reactants are refluxing for 14 hours more, a copious precipitate is formed which is separated, washed and dried.

Organic bases which do not react with formaldehyde (e.g., triethanolamine) may also be used to adjust the  $p_H$  of formaldehyde solutions.<sup>20</sup> Formalin so treated and brought to a  $p_H$  of 5-6<sup>21</sup> may be condensed by progressive addition of urea until a half molar proportion of urea has been added, and the reflux mixture concentrated to a thick syrup. If the  $p_H$  be then brought to 7-7.5, formaldehyde remaining free may be fixed by incorporation of a further quantity of urea or thiourea. If esters of polybasic acids with polyhydric alcohols, which serve as plasticizers, are added, the  $p_H$  of the concentrated product may be lowered to 3.5-5, the resin being then dried *in vacuo* at not too high a temperature (80-140°C., depending on the article to be made). The products, containing formaldehyde and urea approximately in the proportion 1.75:1, may be molded and cured by the application of heat and pressure. By condensing 1 mol of urea with a moderate proportion of formaldehyde (1.05-1.55 mols) at 30°C. in a solution with a  $p_H$  of 4-7, followed by evaporation at 60°C., products useful as molding compositions are obtained.<sup>22</sup> As above, the adjustment of  $p_H$  may be effected by the addition of organic bases, e.g., triethanolamine or guanidine. Substances (e.g., saccharin) which lose their acid character during the reaction have been suggested for the polymerization of the urea-formaldehyde condensates.<sup>23</sup>

Griffith<sup>24</sup> considered that the addition of guanidine confers a much greater

<sup>17</sup> M. C. Dearing, U. S. P. 1,925,795, Sept. 5, 1933, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1933, 27, 5483.

<sup>18</sup> M. C. Dearing, U. S. P. 1,982,794, Dec. 4, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 525.

<sup>19</sup> M. C. Dearing, U. S. P. 1,982,796, Dec. 4, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 525.

<sup>20</sup> French P. 685,945, 1929, to Toledo Scale Mfg. Co.; *Chem. Abs.*, 1930, 24, 6041. British P. 345,935, 1929; *Brit. Chem. Abs. B.*, 1931, 642.

<sup>21</sup> British P. 337,357, 1929, to Toledo Scale Mfg. Co.; *Chem. Abs.*, 1931, 25, 2313. A. M. Howald, Canadian P. 327,690, 1932, to Toledo Scale Mfg. Co., to Toledo Synthetic Products, Inc.; *Chem. Abs.*, 1933, 27, 1219. See also Canadian P. 324,194, 1932; *Chem. Abs.*, 1932, 26, 4669.

<sup>22</sup> British P. 376,807, 1932, to Toledo Synthetic Products, Inc.; *Chem. Abs.*, 1933, 27, 4110. French P. 715,153, 1931; *Chem. Abs.*, 1932, 26, 1731.

<sup>23</sup> French P. 681,400, 1929, to Pfennig Schumacher Werke G.m.b.H.; *Chem. Abs.*, 1930, 24, 4409.

<sup>24</sup> P. W. Griffith, U. S. P. 1,658,597, Feb. 7, 1928, to American Cyanamid Co.; *Chem. Abs.*, 1928, 22, 1244.

latitude as to the  $p_H$  at which condensation may be effected without detriment to the color and transparency of the product. As little as 0.5 per cent of guanidine exercises a marked effect, whereas if 30 per cent of the urea be replaced by guanidine carbonate, hard, colorless resins may be produced by condensation at a  $p_H$  of 4-6. If, however, guanidine be substituted for urea entirely, satisfactory resins may be produced by condensation in a solution of any acidity between the  $p_H$  limits 3-10. When mixtures of urea and guanidine carbonate are employed, the acidity may conveniently be adjusted by addition of acid, using methyl red ( $p_H$  of color change is 5-6) as indicator. The curing of resins containing guanidine is said to proceed more rapidly than with resins containing urea only.

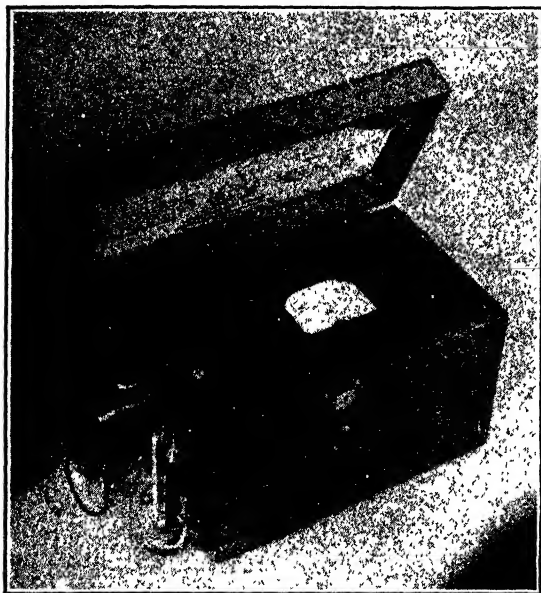


FIG. 96.—  
pH Indicator for Plastic Mixes.

Courtesy Leeds & Northrup Co.

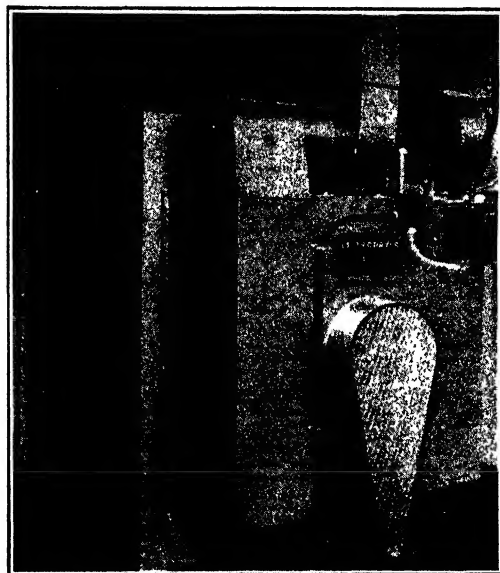
Condensation products that are soluble in water and are reversible gels can be prepared, in the dry state or in solution, by condensing urea and formaldehyde without going beyond the hydrophile stage.<sup>25</sup> The reaction is performed without accelerators, and the dry resulting material dissolves as a clear hydrosol that can be employed in the preparation of varnishes, impregnants or molding powders.

The polymerization or further condensation of dimethylolurea may be carried out by heating a solution or suspension of the compound in the presence of a phosphate, acid potassium oxalate or tartaric acid buffer which maintains the  $p_H$  at 4-7.<sup>26</sup> Such a solution may be circulated through heated tubes where condensation occurs, passing finally into a vacuum spray-drying chamber where the resin is dried to powder form. Buffered suspensions in non-aqueous solvents (monohydric or polyhydric alcohols) may also be employed.

<sup>25</sup> French P. 751,801, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 920. French P. 749,902, 1933; *Chem. Abs.*, 1934, 28, 665. British P. 413,439, 1934; *Chem. Abs.*, 1935, 29, 252.  
<sup>26</sup> M. Luther, U. S. P. 1,947,997, Feb. 20, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2927. British P. 206,875, 1927; *Chem. Abs.*, 1929, 23, 5197. French P. 651,035, 1928; *Chem. Abs.*, 1929, 23, 3315. British P. 320,915, 1928; *Chem. Abs.*, 1930, 24, 2623. C. Heuck and M. Luther, German P. 548,372, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4142.

## ALKALINE CONDENSING AGENTS

The condensation of urea with formaldehyde in the presence of small quantities of basic substances (e.g., barium hydroxide) was found by Einhorn and Hamburger<sup>27</sup> to lead to the formation of dimethylolurea (see Chapter 27). Basic catalysts thus can be used as condensing agents for bringing about the first stage of condensation in the manufacture of urea-formaldehyde resins. Urea may be treated with formaldehyde in the presence of a base, the solution then being neutralized, acidified to bring about gelatinization and poured into molds to solidify.<sup>28</sup> In place of formalin solution, paraformaldehyde may be employed<sup>29</sup>



Courtesy Pittsburgh Lector dryer Corp.

Fig. 97.—Air Dryer for Urea Plastics Temperature and humidity are automatically controlled.

in the presence of just sufficient alkali to bring about condensation as far as the stage of dimethylolurea. The general procedure<sup>30</sup> is to dissolve urea in rather more than 2 mols of formaldehyde, with a small proportion of calcium or barium hydroxide. Dimethylolurea does not immediately separate, and on acidifying the solution with a mineral acid the liquid sets to a white mass with the evolution of heat, becoming quite hard in the course of a short time. The outer layers of a thick mass of the substance are usually translucent, becoming clear on drying *in vacuo* or at room temperature, while the interior is white and opaque. Shrinkage occurs during drying, causing cracking and disintegration of the material. If the mass be poured out and dried in thin layers, the milky solid formed may be pulverized, and may then be molded in a hot press (e.g., under 4000 lb. pressure

<sup>27</sup> A. Einhorn and A. Hamburger, *Ber.*, 1908, 41, 24; *J.C.S.*, 1908, 94 (1), 141.

<sup>28</sup> Carleton Ellis, U. S. P. 1,482,357, Jan. 29, 1924; *Chem. Abs.*, 1924, 18, 911.

<sup>29</sup> Carleton Ellis, U. S. P. 1,482,358, Jan. 29, 1924; *Chem. Abs.*, 1924, 18, 911.

<sup>30</sup> Carleton Ellis, U. S. P. 1,536,882, May 5, 1925; *Chem. Abs.*, 1925, 19, 1966.

at 160°C.) to give transparent materials. A molding pressure higher than that used with most plastics is desirable.

The molding powder thus obtained still contains the acid used for polymerization. This may be washed out, or it may be neutralized by incorporating a small quantity of alkaline material in a mineral filler. The coagulated mass is hard and elastic; it is unaffected by cold water, but disintegrates slowly in boiling water. After molding, the resistance towards water is found to be improved. The clarity of the cured material increases with the completeness of the dehydration of the molding composition.

The degree to which polymerization proceeds, and therefore the plasticity of the product, depends upon the temperature at which condensation occurs. Urea-formaldehyde solutions in contact with zinc carbonate or zinc oxide assume a  $p_H$  of about 6,<sup>31</sup> at which figure condensation proceeds at room temperature, yielding stable solutions of a low degree of polymerization, hardening on long standing to a fusible, crystalline mass which may be dried and hot-molded in the presence of an acid hardening agent. Alternatively, the melted crystalline material may be used to impregnate porous fillers (cellulose, asbestos). The fillers may be introduced into the solution in which condensation actually occurs. The materials so obtained, after hot-pressing, are said to possess higher mechanical strength than those condensed at high temperatures.

By another process,<sup>32</sup> ammonium salts or the salts of aromatic or aliphatic amines are added to the urea-formaldehyde mixture, rendering it acid towards methyl orange but still alkaline to tournesol. Metallic oxides, hydroxides or basic salts may then be introduced to promote condensation. According to Arnaud,<sup>33</sup> the presence of carbohydrates (levulose, glucose, sucrose, dextrin) is advantageous in the process. The incorporation of a proportion of glucose has also been employed by Manesse and Sechehaye<sup>34</sup> and by Israel<sup>35</sup> with zinc oxide as the catalyst. By this method, 2700 g. of 40 per cent formaldehyde are mixed with 1000 g. of urea, 400 g. of glucose and 15 g. of zinc oxide. The reaction, at first endothermic, becomes exothermic. The mixture is heated until 800 cc. of water have distilled, and then concentrated under reduced pressure until 1600 cc. of aqueous distillate have been recovered. At this stage, the material is placed in molds and heated for 36 hours at 80°C. Sugars (glucose and lactose) may also be used as condensing agents and dehydrating compounds in the presence of ammonia or of ammonium salts.<sup>36</sup>

Keller<sup>37</sup> utilized copper sulphate as a catalyst for the initial condensation process. The dry-stage reaction of urea and solid, anhydrous polymers of formaldehyde was carried out by Keller<sup>38</sup> with the aid of a combination of basic and acidic catalysts, and led to the formation of clear, transparent, viscous condensation products. A dry mixture of urea and paraformaldehyde with a small amount of the alkaline catalyst (sodium hydroxide, sodium bicarbonate or other basic salt) is moistened with saturated steam. Then an acid catalyst (e.g., acid sodium phosphate) is introduced and heat is applied to complete the reaction. Calcium chloride<sup>39</sup> and the other alkaline earth chlorides may be used as condens-

<sup>31</sup> R. Armenault, French P. 728,475, 1931, to Fabr. de prod. de chim. org. de Laire; *Chem. Abs.*, 1932, 26, 5778. British P. 386,146, 1933; *Chem. Abs.*, 1933, 27, 4431. See British P. 420,317, 1933; *Brit. Chem. Abs. B*, 1935, 111. U. S. P. 2,004,970, June 18, 1935.

<sup>32</sup> L. Nolet, French P. 690,588, 1929; *Chem. Abs.*, 1931, 25, 1110.

<sup>33</sup> L. Arnaud, French P. 688,269, 1929; *Chem. Abs.*, 1931, 25, 836.

<sup>34</sup> G. C. A. Manesse and J. Sechehaye, British P. 352,283, 1929; *Chem. Abs.*, 1932, 26, 5392.

<sup>35</sup> E. Israel, French P. 695,036, 1929; *Chem. Abs.*, 1931, 25, 2013.

<sup>36</sup> G. C. A. Manesse and J. Sechehaye, French P. 714,388, 1390; *Chem. Abs.*, 1932, 26, 1731.

<sup>37</sup> A. V. Keller, British P. 328,070, 1929; *Chem. Abs.*, 1930, 24, 4175.

<sup>38</sup> A. V. Keller, U. S. P. 1,868,067, July 19, 1932; *Chem. Abs.*, 1932, 26, 5183. British P. 340,373, 1929; *Chem. Abs.*, 1931, 25, 4673. French P. 686,147, 1929; *Chem. Abs.*, 1930, 24, 6042. The initial condensation is also catalysed by sodium chloride, small quantities of inorganic acids and anhydrous oxides of aluminum or thorium (A. V. Keller, British P. 328,938, 1929; *Chem. Abs.*, 1930, 24, 5518).

<sup>39</sup> British P. 359,858, 1931, to Soc. anon. la Ronite; *Brit. Chem. Abs. B*, 1932, 118.



ing agents. Formaldehyde and urea are mixed with 15-60 per cent by weight of calcium chloride, boiled to complete the methylolurea condensation, and finally polymerized by boiling with acid.

#### USE OF FORMALDEHYDE POLYMERS

Urea or thiourea mixed with solid polymerized formaldehyde and fillers, in the absence of water or volatile liquids, yields a product that can be hot-pressed directly.<sup>40</sup> Binding agents, pigments and fire-resistant materials may also be added to the mix. The condensation can be carried out in a melt of organic compounds, which cannot be hardened or which harden only with difficulty,<sup>41</sup> or in a melt of solid hydrocarbons (chlorinated, nitrated or hydrogenated).<sup>42</sup> Among the organic substances used while molten as condensing media are rosin, copal, condensation products of mono- and polyvalent phenols or glycerol esters of phthalic acid, and nitrated, hydrogenated or chlorinated naphthalene as well as phenol-formaldehyde resins.<sup>43</sup>

In the production of molded articles from urea or its derivatives and solid polymerized formaldehyde in fused organic compounds,<sup>44</sup> catalysts added may function either in retarding or accelerating the reaction.<sup>45</sup> For retardation, i.e., to maintain the fluidity of the material for a longer time, basic catalysts (ammonia, calcium hydroxide, hexamethylenetetramine or sodium carbonate) are employed. Acid catalysts, including citric acid, acetic acid, hydrochloric acid and urea nitrate, as well as a number of neutral catalysts accelerate the solidification process, i.e., harden the resin.

Schmidt and Daniels<sup>46</sup> have suggested a molding composition prepared by grinding a mixture containing 110 parts of urea, 110 parts of paraformaldehyde, 150 parts of sulphite fiber and 50 parts of lithopone in a ball mill. The product is then transferred to differential sheeting rolls, where, on continued working, the resin-forming reaction sets in with a considerable rise in temperature. The water formed in the reaction is expelled as it is produced, and the operation is continued until the loss in weight (due to water expulsion) indicates the completion of the reaction. The resulting substance is a dry, sheeted mass, which, on being pulverized, is ready for molding. Additional plasticity is imparted by incorporating high-boiling solvents, e.g., diethyl or dibutyl tartrate or oxalate and halogenated naphthalene derivatives, with the material in the ball mill.

#### HARDENING CATALYSTS

In order to shorten the duration of the actual molding operation and hence lessen labor costs, Ellis<sup>47</sup> recommended the introduction of curing catalysts in the compositions employed. These catalysts may be direct acting (i.e., capable of accelerating the reaction at all times) or they may be latent (active mainly when a certain temperature is reached). Most of the white urea resin molding compositions are disintegrated by protracted heating, and hence the addition of hardening catalysts (especially the latent variety) by shortening the molding time tends to avoid the deterioration of the color and appearance of the article. To prepare

<sup>40</sup> British P. 305,211, 1929, to Bakelite G.m.b.H.; *Brit. Chem. Abs.* B, 1930, 828. British P. 332,964, 1928; *Chem. Abs.*, 1931, 25, 610. German P. 605,107, 1934; *Chem. Abs.*, 1935, 29, 1180. O. Süßenguth, U. S. P. 2,007,987, July 16, 1935, to Bakelite Corp.

<sup>41</sup> British P. 318,883, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1930, 24, 2624. French P. 667,595, 1929; *Chem. Abs.*, 1930, 24, 1189.

<sup>42</sup> British P. 333,398, 1929, to Bakelite G.m.b.H.; *Brit. Chem. Abs.* B, 1930, 997.

<sup>43</sup> O. Süßenguth, U. S. P. 1,996,087, Apr. 2, 1935, to Bakelite Corp.

<sup>44</sup> British P. 318,959, 1929, to Bakelite G.m.b.H.; *Chem. Abs.*, 1930, 24, 2624.

<sup>45</sup> British P. 333,396, 1929, to Bakelite G.m.b.H.; *Chem. Abs.*, 1931, 25, 611.

<sup>46</sup> J. H. Schmidt and R. S. Daniels, U. S. P. 1,917,815, July 11, 1933, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 4640.

<sup>47</sup> Carleton Ellis, U. S. P. 1,905,999, Apr. 25, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 3629.

molding compositions, the initial urea-aldehyde reaction can be carried out in an alkaline medium, subsequent addition of acid controlling the hydrogen ion concentration. During the molding, an added latent catalyst (e.g., amine-hydrochlorides and sodium or barium ethylsulphate) liberates acid and effects the final hardening. Hardening catalysts may also be employed in urea resins containing cellulosic fillers. Thus, a secondary charge of wood flour is impregnated with the acid catalyst and added to the resin binder. Catalysts introduced in this manner do not come into active contact with the urea resin until the latter is molded. Protected in this manner, the acid is held in virtually an inactive state until the flow of the resin during hot pressing causes dissemination of the acid component with consequent increase in the rate of curing.



FIG. 98.—  
Translucent Light Fixtures  
of Beetle Urea Resins.

*Courtesy Modern Plastics*

Substances, exemplified by phthalic acid,  $\beta$ -bromohydrocinnamic acid and isodibromosuccinic anhydride which dissolve when the resin melts, producing acidity, were incorporated by Howald<sup>48</sup> together with plasticizers (e.g., natural or alkyd resins) in urea molding powders. In this way, 1 mol of urea was refluxed 30 minutes with 2.25 mols of formaldehyde to which triethanolamine had been added.<sup>49</sup> The mixture was partially evaporated, more urea added and evaporation completed. The ground product was mixed with a polybasic acid-polyhydric alcohol resin containing an excess of free acid, and sufficient urea was added to give the ratio 1 mol of urea to 1.5 or 2 mols of formaldehyde.

The water usually present under molding conditions is used, by Eaton,<sup>50</sup> to react with a neutral organic substance to liberate acid *in situ*, e.g. addition of 0.25-1 per cent of dimethyl oxalate is recommended. A small proportion (about 3 per cent) of a mixture of various plasticizers may be added to assist the flow during molding.<sup>51</sup>

<sup>48</sup> A. M. Howald, British P. 312,343, 1928, to Toledo Scale Mfg. Co.; *Chem. Abs.*, 1930, 24, 982. French P. 672,851, 1929; *Chem. Abs.*, 1930, 24, 2317. Canadian P. 324,194, 1932, to Toledo Synthetic Products, Inc.; *Chem. Abs.*, 1932, 26, 46-9. Canadian P. 341,536, 1934; *Chem. Abs.*, 1934, 28, 4849. German P. 603,434, 1934; *Chem. Abs.*, 1935, 29, 524.

<sup>49</sup> British P. 337,357, 1929, to Toledo Scale Mfg. Co.; *Chem. Abs.*, 1931, 25, 2313. British P. 345,935, 1929; *Brit. Chem. Abs. B.* 1931, 642. British P. 312,343, 1930; *Brit. Chem. Abs. B.* 1931, 73.

<sup>50</sup> M. M. Eaton, British P. 358,470, 1930, to Pollopas, Ltd.; *Chem. Abs.*, 1932, 26, 6106. French P. 718,094, 1931; *Chem. Abs.*, 1933, 27, 1531.

<sup>51</sup> M. M. Eaton, British P. 358,075, 1930, to Pollopas, Ltd.; *Chem. Abs.*, 1933, 27, 436. French P. 718,094, 1931; *Chem. Abs.*, 1933, 27, 1531.

Salts of hexamethylenetetramine may be added as accelerators,<sup>53</sup> and a solid organic acid (oxalic acid) incorporated with the mass while the material is being ground. Plastic compositions containing an acid accelerator are said to be preserved without alteration by incorporating, in the composition, hexamethylene-tetramine in excess of the total amount of acid present.<sup>54</sup>

As an alternative to the process of grinding the dried polymerization product, the material may be obtained in finely divided form by spraying the solution against a current of warm air at 40-50°C.<sup>54</sup> Such a process applied to the hydrophile condensation product of less than two mols of formaldehyde with 1 mol of urea yields a product which may be mixed with ammonium sulphate to accelerate hot-pressing. According to Pollak and Kraus,<sup>55</sup> it is very desirable that molding compositions should have a low degree of polymerization and be free from excess formaldehyde. Premature polymerization may be brought about either by drying at too high a temperature, or by the action of excess of acid in the preparation of the resin. The amount of acid or acid salt used should therefore be rigidly restricted and drying is best performed *in vacuo*. Spray drying can be used to dehydrate the finely comminuted product. The deleterious effect of free formaldehyde is overcome by the addition to the molding powder of ammonium salts, e.g., 0.5-2 per cent of ammonium sulphate, in a dry state. The time occupied in the molding operation may also be cut down by carrying out only partial polymerization within the mold, followed by a more prolonged heating process outside the mold to complete curing.

A urea-formaldehyde product in the preliminary stage of its condensation is sometimes dissolved in a solvent (dichlorohydrin), mixed with a filler and converted to an insoluble form by heating.<sup>56</sup>

#### USE OF WATER TO INCREASE FLOW

A method of producing transparent plates from urea-formaldehyde condensation products was developed by Goldschmidt and Beuschel.<sup>57</sup> In this process, thin, dry plates of the condensation product are treated for a short time with a liquid or vapor not acting as a binder (e.g., with water or with a water-soluble organic liquid that is not a solvent for the condensation product). The plates are then superimposed and united by heat and pressure.

The function of water in increasing the flow properties of urea-formaldehyde resins is emphasized in the work of Landecker.<sup>58</sup> The urea-formaldehyde resins resemble protein-like masses such as casein, horn or glue in that they all show an excellent plasticity when molded with sufficient added water. Thus, a powdered urea-formaldehyde molding material acquires a satisfactory fluidity on the addition of about 5 per cent by weight of water. The resulting plasticity enables the moistened powder to flow under a pressure of less than 1000 pounds per square inch and allows the overflow to be rapidly squeezed out of the mold. This is considered to be advantageous since, according to Landecker, urea resins normally require a pressure of 4000 pounds per square inch for manufacturing even small and simple articles. In place of water, a salt that yields water of crystallization may be employed, and other liquids such as those which serve as plasticizers for natural albuminous substances

<sup>53</sup> E. C. Rossiter, British P. 351,093, 1930, to British Cyanides Co., Ltd.; *Chem. Abs.*, 1932, 26, 5392.

<sup>54</sup> French P. 714,101, 1931, to British Cyanides Co., Ltd.; *Chem. Abs.*, 1932, 26, 1731. German P. 586,543, 1933; *Chem. Abs.*, 1934, 28, 2480. E. C. Rossiter and A. Brookes, British P. 359,498, 1930, *Chem. Abs.*, 1933, 27, 381. German P. 564,914, 1931; *Chem. Abs.*, 1933, 27, 1222.

<sup>55</sup> British P. 328,040, 1928, to Kunstharzfabr. F. Pollak G.m.b.H.; *Brit. Chem. Abs. B*, 1930, 677.

<sup>56</sup> F. Pollak and W. Kraus, U. S. P. 1,935,411, Nov. 14, 1933, to Synthetic Plastics Co., Inc.; *Chem. Abs.*, 1934, 28, 591. British P. 291,366, 1927, to Kunstharzfabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1929, 23, 3782.

<sup>57</sup> French P. 654,554, 1928; *Chem. Abs.*, 1929, 23, 3782.

<sup>58</sup> British P. 369,571, 1929, to Bakelite G.m.b.H.; *Chem. Abs.*, 1933, 27, 3096.

<sup>59</sup> S. Goldschmidt and W. Beuschel, German P. 553,161 1929; *Chem. Abs.*, 1932, 26, 4690.

<sup>60</sup> M. Landecker, U. S. P. 1,904,243, Apr. 18, 1933; *Chem. Abs.*, 1933, 27, 3300.

(e.g., alcohols, amines or ketones) are also used. Instead of adding water to the dried molding composition, the wet condensation mass may be dried on hot rollers until the proper moisture content (10-20 per cent) is obtained. The water-containing urea-aldehyde resin may be molded at 110° with a pressure of 700-1000 pounds per square inch.

Ellis<sup>80</sup> found that the flow of urea resin molding compositions could be improved by slightly moistening with water. The water is atomized into the pulverized material while the latter is being agitated. The resulting product is not of the best grade, however, and the process is not recommended for the production of high-quality articles.

The use of 5 per cent of water, alcohol, ketones or amines with powdered urea-aldehyde resins to increase the fluidity was suggested by other workers.<sup>80</sup> Fillers, pigments and glycerol or other moisture-absorbing substances may also be added. A similar treatment serves for thiourea resins.

#### MOLDING COMPOSITIONS WITH CELLULOSIC FILLERS

Although shaped articles made from clear, glass-like urea-formaldehyde condensation products are not likely to be permanent<sup>81</sup> (see Chapter 27), conditions are quite different when a substantial proportion of cellulose is present with the urea. There is definite indication of an affinity between urea resin condensates and cellulose. It is probable that between cellulose and urea resin there exists a combination explainable on the basis of secondary valence or covalence. So definite are the indications of chemical combination of the recognized type or of the various reactions resulting from covalence affinities that the author has given the term "urea-formaldehyde cellulosate" to the product obtained.<sup>81a</sup> It suffices to say that the compositions which contain a considerable proportion of cellulose incorporated with the urea-formaldehyde condensation products are permanent as compared with the clear glass products in which the cellulose is absent.

The cellulosic fillers may be used either in the crude form, as wood flour, or the purified type (paper, cotton flock or  $\alpha$ -cellulose in sheet form).<sup>82</sup> The urea-formaldehyde resin, as a syrup, should contain sufficient water to impregnate the cellulose fibers completely and is best added while hot. Impregnation is conveniently carried out by running the resin syrup into an evacuated vessel containing the cellulose and then applying 50-100 lb. pressure. The canals of the fibers are in this manner completely filled. For the preparation of molding compositions, the dried material should be ground fine, inorganic pigments being added at this stage.

Non-discoloring mold lubricants represented by zinc, magnesium or calcium stearates, to the extent of less than 1 per cent, may be incorporated during grinding, and the compositions molded under 1000-3000 lb. per square inch at 110-150°C. For white objects, the desirable maximum temperature is about 130°C., while 150°C. usually should not be exceeded owing to the risk of blistering. The tendency to blister is greatly reduced by cellulose, which acts as something more than a mere filler. Mechanically held water is well removed by the drying process. The water present within the mold, which may give rise to blistering, is produced by the condensation reactions constituting the curing step. Cellulosic materials, especially hydrocellulose, which may have become partially dehydrated during

<sup>80</sup> Carleton Ellis, U. S. P. 1,905,999, Apr. 25, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 3629.

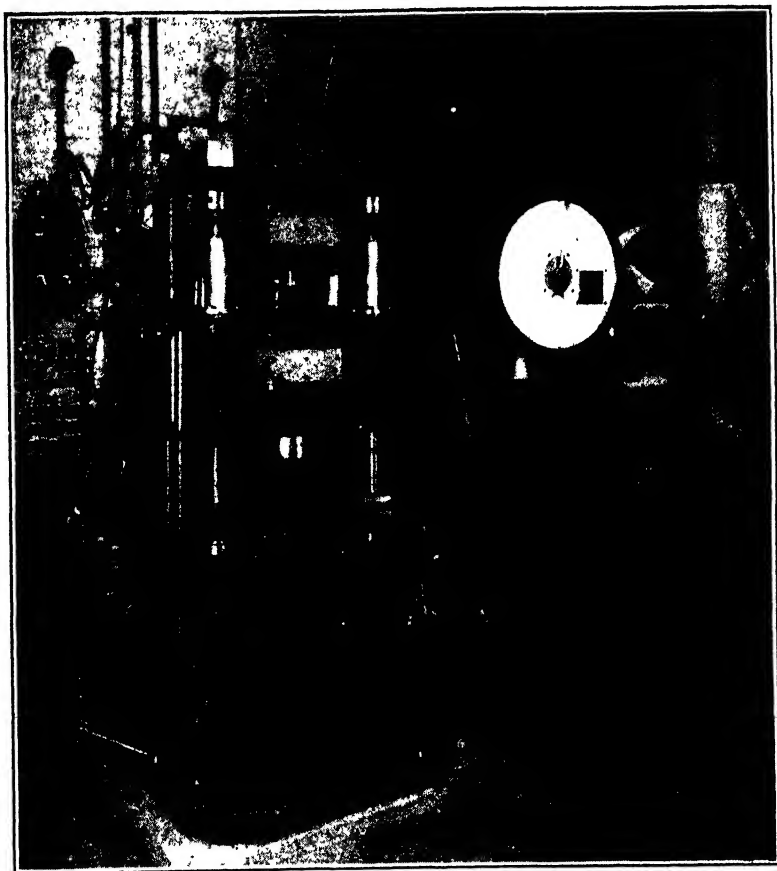
<sup>81</sup> British P. 812,650, 1928, to Pfenning-Schumacher-Werke Ges.; *Chem. Abs.*, 1930, 24, 981. French P. 675,841, 1929; *Chem. Abs.*, 1930, 24, 2905.

<sup>81a</sup> G. Payras (*Rev. gén. mat. plastiques*, 1933, 9, 79; *Chem. Abs.*, 1933, 27, 2590) stated that cracks in articles made from urea-formaldehyde resins are caused by the presence of free acid, primarily.

<sup>82</sup> Briefly termed a *glucanure*.

<sup>80</sup> Carleton Ellis, U. S. P. 1,905,999, Apr. 25, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 3629.

drying, are able to take up a large part of this moisture thereby inhibiting blistering. Acid salts, such as sodium hydrogen sulphate, are active catalysts of the curing process, and may be incorporated in latent form as sodium ethyl sulphate which decomposes hydrolytically in the hot press. Translucency of the pressed product is promoted by thorough incorporation of the resin syrup with the cellu-



*Courtesy Toledo Synthetic Products, Inc.*

FIG. 99.—An Automatic Precision Testing Device for Plastic Flow. This instrument measures and records the pressure required to flow thermosetting plastic compositions throughout the duration of plasticity.\*

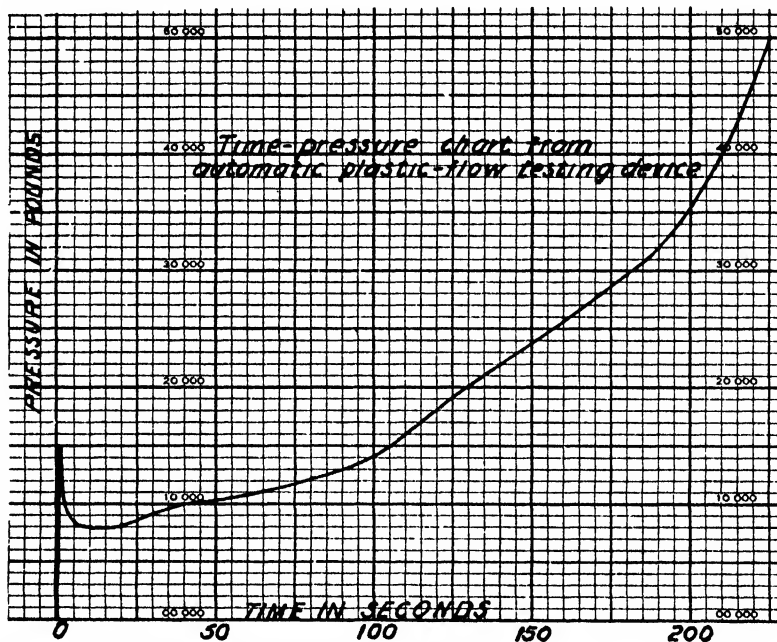
\* Instrument manufactured by Toledo Precision Devices, Inc.

lose, and careful and complete drying. Mineral pigments should be absent<sup>62a</sup> for best results, as should more than a small percentage of mold lubricant. The use of high pressures during molding (2000-3000 lb.) is advantageous.

Cellulose-urea resins made in this manner are employed for a great variety of products; viz., molded articles and sheets, extruded rods and tubes and veneered stock. Resistance to water is enhanced by the incorporation of a proportion of thiourea, as little as 10 per cent having a marked effect.

<sup>62a</sup> A small proportion of a white pigment such as titanium oxide or lithopone is sometimes used in conjunction with a much larger proportion of cellulose, in making light-colored molded articles.

A valuable property of resins of this type is the possibility of making materials containing a relatively high proportion of cellulose by a two-stage process. Just sufficient cellulose may first be added to absorb completely the resin syrup, e.g., 40 parts of wood flour to 60 parts of resin solids, and this material is dried. The dried impregnated material is then ground with an additional quantity of unimpregnated cellulose, and as a result the finished molding composition may contain as little as 15 per cent of resin solids. In this manner, the prolonged drying of large masses of impregnated cellulose and possible difficulties from incomplete drying due to formation of incrustations are avoided. Moreover, curing catalysts



*Courtesy Toledo Synthetic Products, Inc.*

FIG. 99a.—A Typical Time-Pressure Chart (of a Urea Resin) Obtained with Apparatus Shown in Fig. 99. Graph indicates the pressure necessary to flow the thermosetting composition in various stages of cure.

may be added in disseminated form as impregnants of the secondarily added cellulose. Boric acid, phosphoric acid, phosphomolybdic acid and other inorganic acids, acid salts and non-volatile organic acids serve as catalysts for the purpose. The use of a well-dried secondary charge of cellulose is especially helpful in absorbing liberated water, assisting in avoidance of blistering. During the curing step, some solution or absorption of the cellulose occurs, since the ligneous structure appears to be largely destroyed. Products obtained from cedar-wood flour differ from those produced from pine or spruce woods.

As an example of the production of such compositions, 840 parts of urea are mixed while cold and refluxed for 10 minutes with 2400 parts of 37 per cent formaldehyde of  $p_H$  5.6. Next, 300 parts of thiourea are added, and the boiling continued for 20 minutes. The liquid is poured over 730 parts of wood flour, and the mass dried at 30-50°C. on Monel metal screens. The dried material is ground to pass a 40-mesh sieve, and then molded at 100-130°C. under 1500 lb. pressure, giving a light brown, translucent product.

Derivatives of cellulose (cellulose esters) were employed by Nash<sup>66</sup> as filling materials in the reaction of urea and solid polymers of formaldehyde. Cellulose acetate (32 parts) is admixed with 94 parts (by weight) of urea, 94 parts of paraformaldehyde and 100 parts of wood flour. After thorough mixing, the material is transferred to differential mixing rolls and sheeted. The resin formation takes place during this operation, after which the sheets are crushed and pulverized for use as a molding powder. Additional plasticity is imparted to the product by adding ethylene glycol, naphthalene or the di-alkyl esters of oxalic, tartaric or phthalic acid to the original mix. Other additions, including natural or synthetic resins, substances capable of reacting with uncombined formaldehyde, high-boiling organic compounds to increase the flexibility and materials that bind the water formed in the reaction, may be made.<sup>64</sup> The progress of the resin formation is retarded by ammonia, hexamethylenetetramine, calcium hydroxide and sodium carbonate, and is accelerated by acids or acid salts.<sup>65</sup> Lougovoy<sup>66</sup> used urea-aldehyde resins together with nitrocellulose and an organic solvent for molding.

#### VARIOUS APPLICATIONS OF UREA RESINS IN MOLDING

The urea-aldehyde resins have been applied in various other fields of hot-molding in addition to those already outlined. Waste wood, peat or lignin mixed with urea-aldehyde condensation products and molded under heat and pressure give insulating and coating materials.<sup>67</sup> Eisenmann and Bergmann<sup>68</sup> described a process for making electromagnet cores of high permeability by pressing a mixture of a urea-formaldehyde resin and iron powder (made by the thermal decomposition of iron carbonyl).

As an example, 4 kg. of iron powder are mixed in a kneading machine with 330 g. of an ethyl alcohol solution (36 per cent strength) of a condensation product of urea and formaldehyde, diluted with 800 g. of a mixture containing equal parts (by volume) of ethyl alcohol and benzene. After mixing, the solvent is entirely driven off by heating to about 80°C. *in vacuo*. The impregnated iron powder is formed into rings by a pressure of 7000 kg. per square centimeter in a mold. A core constructed from 3 such rings and provided with a single layer of winding has a specific gravity of 6.4 and a permeability ( $\mu$ ) of 35.2

Molds for producing printing surfaces, which may be used for casting type metal or for the production of rubber stamps or dies, are made from a mixture of urea-formaldehyde resin and graphite with other fillers (e.g., cellulose or asbestos).<sup>69</sup> A molding composition for making buttons is prepared by condensing urea with formaldehyde and adding an amount of starch or flour that is a multiple of the weight of urea used.<sup>70</sup> The mixture is pressed at room temperature or at a raised temperature. Other resins and softening agents (wool fat) may be added.

A method of preparing materials used in laminated products was described by Stockfisch.<sup>71</sup> The material consists of a paper base impregnated with urea-resin varnish. Calendered paper is run through the urea resin solution and then through

<sup>66</sup> C. A. Nash, U. S. P. 1,721,742, July 23, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 4584. Canadian P. 321,191, 1932; *Chem. Abs.*, 1932, 26, 3344. British P. 327,969, 1929; *Chem. Abs.*, 1930, 24, 5173. French P. 670,841, 1929; *Chem. Abs.*, 1930, 24, 1946. German P. 579,553, 1933; *Chem. Abs.*, 1934, 28, 1154.

<sup>64</sup> British P. 305,211, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1929, 23, 4837. British P. 318,883, 1928; *Chem. Abs.*, 1930, 24, 2624.

<sup>65</sup> British P. 318,959, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1930, 24, 2624.

<sup>66</sup> B. N. Lougovoy, U. S. P. 1,922,690, Aug. 15, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 5150.

<sup>67</sup> French P. 697,312, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3100.

<sup>68</sup> K. Eisenmann and F. Bergmann, U. S. P. 1,783,561, Dec. 2, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 389. German P. 565,664, 1928; *Chem. Abs.*, 1933, 27, 2542. British P. 319,854, 1929; *Chem. Abs.*, 1930, 24, 2847. French P. 734,687, 1932; *Chem. Abs.*, 1933, 27, 941.

<sup>69</sup> M. Smith, British P. 365,126, 1930, to Anglo Pencil Co., Ltd. and Pollopos, Ltd.; *Chem. Abs.*, 1933, 27, 2052.

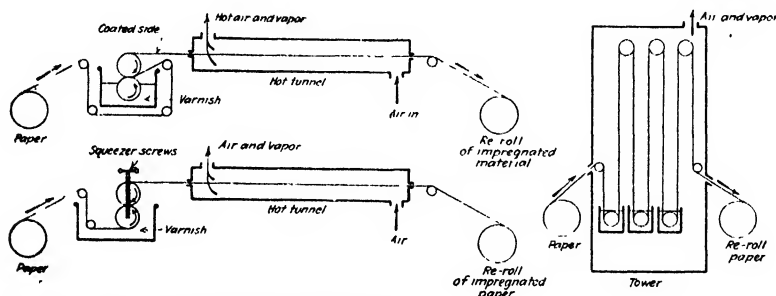
<sup>70</sup> I. Thorn, British P. 287,727, 1927, to Silur Techn. & Chem. Prod. G.m.b.H.; *Chem. Abs.*, 1929, 23, 489. Austrian P. 125,966, 1930; *Chem. Abs.*, 1932, 26, 2287. French P. 632,526, 1927; *Chem. Abs.*, 1928, 22, 3499.

<sup>71</sup> H. E. Stockfisch, *Chem. Met. Eng.*, 1934, 41, 302.

a tunnel system against a current of heated air which is controlled by an arrangement of steam pipes and baffle louvres (see Fig. 100). The paper passes through the varnish at a speed of 100 inches per minute with the tunnel temperature at 80°C. Squeezer rolls which force the varnish into the fibers control the accuracy of the resin content. A tower system embodying successive dips of the paper in the solution may also be employed. The impregnated papers are molded under heat and pressure.

Matches that can be repeatedly ignited by friction and extinguished were developed by Ringer<sup>73</sup> using a urea-aldehyde resin as a base. The slow-burning material has an igniting composition distributed in the resin base which is then molded into rods and coated with water glass. Pentamethylenediaminedisulphine (obtained from ammonium sulphide and formaldehyde) may be used with urea-formaldehyde condensation products in producing plastic-molding compositions.<sup>74</sup> Urea-formaldehyde resin compositions are also used in the hot molding of boxes.<sup>74</sup>

The problem of decorating urea ware (a term applied to molded urea-aldehyde products manufactured for domestic purposes) was studied by Froesé.<sup>75</sup> These



Courtesy Chemical and Metallurgical Engineering

FIG. 100.—Tunnel and Tower Systems Devised for the Impregnation of Fabrics or Paper with Urea Resin Varnishes. (H. E. Stockfish)

articles are normally decorated by applying to their surfaces decalcomanias or oil-pigments, which are easily effaced. Froesé found that the molded urea articles scorched when pressed against a sufficiently hot body and that the resin swelled if allowed to absorb intense heat. By using a properly shaped die at a temperature of about 650°C., any design can be burnt into the resin surface, leaving a bleached, raised border as an outline for the design.

A bonding composition is made by mixing coagulated rubber with a liquid urea-formaldehyde condensation product and heating (at a temperature below the hardening point of the urea resin) until the composition flows.<sup>76</sup> The rubber is thereby dispersed in the heat-hardenable liquid, and the composition serves as a bond for abrasive grains and other fillers. The recording layer of sound records may be made from a composition consisting of phenol and urea resins and not more than 20 per cent of inorganic and organic fillers in colloidal form (e.g., kaolin, steatite, graphite and nitrocellulose, or gelatin dissolved in glycerol).<sup>77</sup> Loudspeaker diaphragms are made by molding, under heat and pressure (about 800 kg. per sq. cm.), a solid polymer of formaldehyde and a urea in a broken or powdered form.<sup>78</sup>

<sup>73</sup> F. Ringer, British P. 369,621, 1930; *Chem. Abs.*, 1933, 27, 2581.

<sup>74</sup> British P. 358,089, 1930, to Dr. Thomas & Co., G.m.b.H.; *Brit. Chem. Abs. B*, 1931, 1147.

<sup>75</sup> H. M. L. M. Smith, British P. 323,759, 1928, to Rolls Razor, Ltd.; *Chem. Abs.*, 1930, 24, 3388.

<sup>76</sup> E. Froesé, U. S. P. 1,914,247, June 13, 1933; *Chem. Abs.*, 1933, 27, 4369.

<sup>77</sup> British P. 463,698, 1933, to Carborundum Co., Ltd.; *Chem. Abs.*, 1934, 28, 3850.

<sup>78</sup> British P. 373,926, 1931, to Steatit-Magnesia A.-G.; *Brit. Chem. Abs. B*, 1932, 737.

<sup>79</sup> British P. 406,327, 1934, to Lohusta Electro-Akustik G.m.b.H.; *Chem. Abs.*, 1934, 28, 4882.



A laminated pulp product described by Kienle and Scheiber<sup>79</sup> is produced by forming layers of interlocked fibers of wet paper pulp containing urea-formaldehyde resins. Fillers and pigments are added, and the material is dried and hot-molded.

Disintegrated cork can also be incorporated with up to 30 per cent of its weight of unhardened urea-aldehyde resin and molded under heat and pressure.<sup>80</sup> Other fillers including wood flour or lignin may be similarly impregnated and hardened in the press.<sup>81</sup> Catalysts, casein, horn, yeast and aldehydes are also added, the product being used as an electrical insulating material.



Courtesy Unyte Corporation

FIG. 101.—Non-Shatterable Cup, Juice-Strainer, Coffee Guide and Paper-Cup Holder Molded of Unyte in Colors.

Vulcanized fiber can be made impermeable to water by treatment with a urea-formaldehyde resin.<sup>82</sup> Urea (30 parts) is dissolved in 100 parts of water, and vulcanized fiber is allowed to swell in this solution until it ceases to absorb any more of the liquid. The mass of vulcanized fiber, saturated with urea solution, is immersed in a 30 per cent solution of formaldehyde for 1-2 days. Catalysts (acids, bases or salts) may be added to the formaldehyde. The fiber is then dried and is heated at 90-95°C. for from a few hours up to several days, according to the dimensions of the articles

Keller<sup>83</sup> described the use of decorated sheets of fabric or paper impregnated with a viscous urea-formaldehyde resin solution for molding in or upon previously molded articles for the purpose of ornamentation. The impregnated material is

<sup>79</sup> R. H. Kienle and W. J. Scheiber, British P. 393,412, 1933, to Brit. Thomson-Houston Co.; *Chem. Abs.*, 1933, 27, 5910.

<sup>80</sup> British P. 322,752, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2847. French P. 675,898, 1929; *Chem. Abs.*, 1930, 24, 2846.

<sup>81</sup> British P. 232,635, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 3747.

<sup>82</sup> British P. 816,700, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 892. French P. 654,411, 1928; *Chem. Abs.*, 1929, 23, 3808.

<sup>83</sup> A. V. Keller, British P. 333,763, 1929; *Chem. Abs.*, 1931, 25, 610.

given a preliminary drying before carrying out the molding operation. A cellulosic carrier for the design and color may also be impregnated with a urea-formaldehyde resin and subjected to heat and pressure in layers with other cellulose substances.<sup>84</sup> This operation brings the cellulosic material into "colloidal suspension" in the resin, and all that remains visible is the applied design and color. Electrical insulating parts including switch gears, fuse components and magneto distributors can be

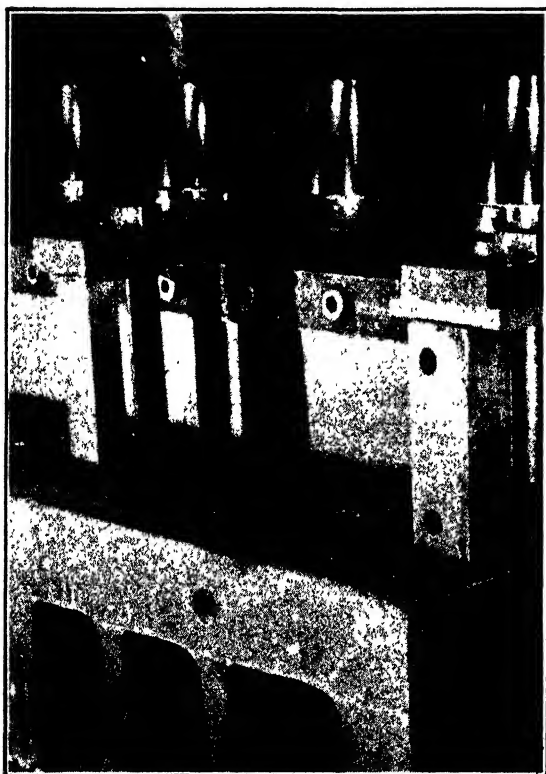


FIG. 102.—  
Molds for Bottle Caps.

*Courtesy American Cyanamid and  
Chemical Corp.*

formed by molding wood flour, paper pulp, asbestos or cotton flock with a urea-aldehyde resin.<sup>85</sup>

Urea-formaldehyde condensation products are used with cellulose to form paper and cardboard products.<sup>86</sup> The dried, powdered condensation product (150 parts) is mixed in a pulping machine with 100 parts of sulphite-whitened cellulose (calculated on a dry-weight basis) and the necessary amount of water. The cellulose is crushed until the desired fiber length is obtained. The mixture is then diluted and transformed into paper in an ordinary paper-making machine. The dried papers can be shaped at 145°C. with a pressure of 150 kg. per sq. cm., forming

<sup>84</sup> British P. 375,791, 1932, to H. Römmler A.-G.; *Chem. Abs.*, 1933, 27, 3837.

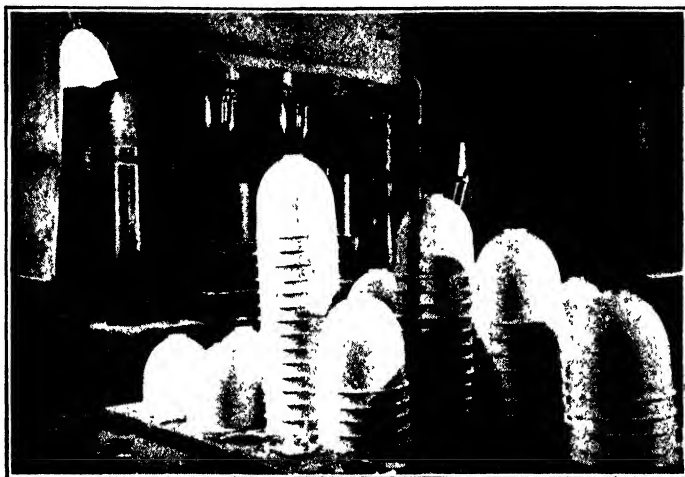
<sup>85</sup> W. E. Pattman, British P. 354,174, 1930, to Bakelite, Ltd.; *Chem. Abs.*, 1933, 27, 357.

<sup>86</sup> French P. 758,458, 1934, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 3233. Swiss P. 163,902, 1933; *Chem. Abs.*, 1934, 28, 2860.

homogeneous molded objects. A single leaf of this material (or a few leaves pressed together) is said to be flexible and translucent. By using many layers, a tenacious, homogeneous, laminated material is obtained.

#### COMMERCIAL MOLDING COMPOSITIONS

A considerable use for urea resin molding compositions has been in the production of dish ware, including tableware of various sorts, and drinking cups (see Fig. 101); the relatively unbreakable quality of such moldings making them superior to glass for many purposes (see Fig. 102). On the other hand, unlike glass, such containers do not resist the high temperatures of a domestic oven sufficiently to be used for baking purposes. Urea resins are also extensively em-



<sup>1</sup>Courtesy American Cyanamid and Chemical Corp

FIG. 103.—Light Shades from Urea Resins; Forming Press in Background.

ployed in the button industry where their strength and resistance to washing make them superior to casein and vegetable ivory.<sup>87</sup> Since urea resins are odorless and possess chemical stability and mechanical strength, they are being used as caps and closures for jars and bottles.

The properties of commercial urea molding compositions may be illustrated by a consideration of the product known as Unyte.<sup>88</sup> This resin is sold in the form of granulated or powdered stock. Unyte is stable during storage, has an especially rapid curing time and can be manufactured in a variety of light-fast shades ranging from white through delicate pastel tints to black (see Fig. 103). During the molding of this product the flow can be easily controlled.

A urea-formaldehyde or urea-thiourea-formaldehyde molding powder known as "Beetle"<sup>88a</sup> is used in the manufacture of dishes, cups, a wide variety of household articles, automobile hardware and plumbing and electrical fixtures.<sup>89</sup> From this material molded articles can be made possessing light colors and an attractive

<sup>87</sup> Carleton Ellis, *Ind. Eng. Chem.*, 1934, 26, 38.

<sup>88</sup> Unyte is a product of the Unyte Corporation. See *Plastics and Molded Products*, 1932, 8, 76. See also *Chem. Met. Eng.*, 1935, 42, 43.

<sup>88a</sup> A product of Synthetic Plastics Co.

<sup>89</sup> *Molded Products*, 1929, 5, 95. See also A. C. Blackall, *Plastics*, 1927, 3, 606; 1928, 4, 200.

translucent appearance. The material can be formed into very thin layers and shapes. Special precautions must be taken to exclude dust during processing, and, in the case of powders containing thiourea, staining of molds must be avoided. Thiourea stock is molded in stainless steel or chromium-plated molds at 140-145°C. under pressures varying from 1500 to 3000 pounds per square inch. The curing time is usually 3-7 minutes, from 50 to 100 per cent longer than the phenolic molding compositions. The specific gravity of the molded product is reported to be 1.49

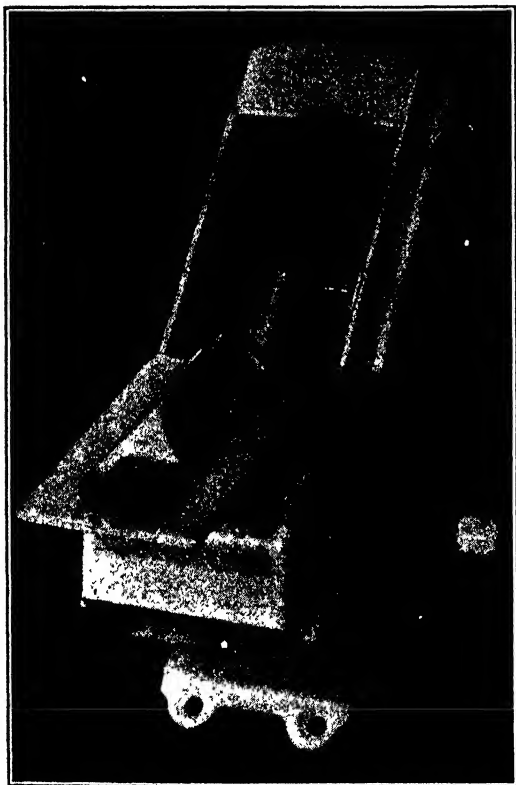


FIG. 104.—  
Chime Housing Molded from  
Beetle Urea Resin.

*Courtesy Modern Plastics*

and the tensile strength 5000-6000 lb. per square inch. Since the products are resistant to corrosion, one suggested use is as fittings in steamships, where attack by salt spray normally presents a serious problem.

Another molding composition of the urea-formaldehyde type is known as "Plaskon."<sup>90</sup> This material is unaffected by alcohol, acetone, oils or other common solvents, and the water absorption at 20°C. is 0.07-0.86 per cent in 24 hours. It is moderately resistant to cold, dilute acids, but is attacked by hot or concentrated acids. It also resists cold, dilute alkalies and hot, very dilute alkalies (soap, borax and cleaners). The specific gravity of the product is 1.43 and the dielectric strength (puncture) is 300-400 volts per mil.

A molding composition was prepared, by Pollak and Ripper,<sup>91</sup> by incorporating

<sup>90</sup> A. M. Howald, *Chem. Met. Eng.*, 1931, 38, 583. Plaskon is made by Toledo Synthetic Products, Inc. See also *Chem. Met. Eng.*, 1932, 39, 654.

<sup>91</sup> K. Ripper, U. S. P. 1,625,283, April 19, 1927, to F. Pollak; *Brit. Chem. Abs. B*, 1927, 532.

the viscous initial condensate of urea, thiourea and formaldehyde with fibrous fillers and pigments. The resulting material is hot-pressed at pressures of 150-300 kg. per square centimeter and given an additional air or vacuum drying.

#### RECOVERY OF SCRAP RESIN

The recovery of usable resin from the waste material of a molding plant or from splinters and borings obtained in the working of cured resin articles is an important economic factor especially in countries producing much turnery ware. The hardened material may be made soluble<sup>52</sup> by heating under pressure with more than an equal weight of formaldehyde solution at 120°C. for 2-3 hours. A thick solution is thereby obtained, which is diluted and boiled with a further quantity of urea, and subsequently processed as new material.

The cured resin may also be heated with aldehyde in the presence of acids,<sup>53</sup> or heated with the intermediate condensation product still containing free formaldehyde. It is also stated to be possible to mix the finely comminuted scrap material directly with formaldehyde and to use the product as a molding powder.

Ripper<sup>54</sup> described the use of mineral acids for resin recovery. The finely divided cured resin, boiled with 10 per cent hydrochloric or nitric acid, passes readily into solution, and on cooling or dilution is thrown down as a bulky precipitate which may be separated and dried. This powder is then brought into solution by formaldehyde or by mechanical dispersion in water with a colloid mill. The solutions are utilized as varnishes and impregnants, while the recovered powder is employed as a filling agent for the urea-formaldehyde resins made in the usual way.<sup>55</sup> Used for this purpose, resins are obtained from which water is expelled more readily, and which are said to harden faster than with unmixed material. Ammonium salts, which react with liberated formaldehyde and set free acid, may also be used as solubilizing agents, as may acid chlorides and acid salts. The solubilizing agents need be present in only limited quantity, as solution of the material is not required to be complete.<sup>56</sup> Thus, comminuted, cured resin can be merely swelled with hydrochloric acid and converted into a homogeneous material with heat and pressure.

U. S. P. 1,460,606, July 3, 1923; *J.S.C.I.*, 1923, 42, 940A. British P. 344,872, 1929; *Brit. Chem. Abs.* B, 1931, 598. French P. 683,327, 1929; *Chem. Abs.*, 1930, 24, 4597. F. Pollak, U. S. P. 1,458,543, June 12, 1923; *J.S.C.I.*, 1923, 42, 940A. Austrian P. 109,532, 1928; *Chem. Abs.*, 1929, 23, 942. British P. 181,014, 1922; *J.S.C.I.*, 1923, 42, 988A. This molding composition is known as "Pollopas." Porous molds were suggested for use with this material (K. Ripper, U. S. P. 1,701,986, Feb. 12, 1929, to F. Pollak; *Chem. Abs.*, 1929, 23, 1518. F. Pollak, British P. 217,838, 1923; *Chem. Abs.*, 1925, 19, 384. F. Pollak and K. Ripper, *Chem.-Ztg.*, 1924, 48, 569, 582; *J.S.C.I.*, 1924, 43, 878B). O. Manfred and J. Obrist (*Z. angew. Chem.*, 1928, 41, 971; *Chem. Abs.*, 1928, 22, 4674) found that plates molded from Pollopas had a higher modulus of elasticity than plates from Bakelite.

<sup>52</sup> A. Gams and G. Widmer, U. S. P. 1,679,246, July 31, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1928, 22, 3792. German P. 499,589, 1925; *Chem. Abs.*, 1930, 24, 4597. British P. 246,127, 1926; *Brit. Chem. Abs.* B, 1927, 684. Canadian P. 281,326, 1928; *Chem. Abs.*, 1928, 22, 3270. German P. 487,308, 1925; *Chem. Abs.*, 1930, 24, 2256. French P. 609,108, 1926; *Brit. Chem. Abs.* B, 1927, 228.

<sup>53</sup> W. S. Rothera, S. Blythen and H. R. Gillespie, German P. 525,285, 1925; *Chem. Abs.*, 1931, 25, 4096.

<sup>54</sup> K. Ripper, U. S. P. 1,817,931, Aug. 11, 1931, to Pollopas, Ltd.; *Chem. Abs.*, 1931, 25, 5525. F. Pollak, British P. 240,840, 1924; *Chem. Abs.*, 1926, 20, 2233.

<sup>55</sup> K. Ripper, U. S. P. 1,817,940, Aug. 11, 1931, to Pollopas, Ltd.; *Chem. Abs.*, 1931, 25, 5525. Canadian P. 276,324, 1927; *Chem. Abs.*, 1928, 22, 2037.

<sup>56</sup> F. Pollak, British P. 266,389, 1924; *Chem. Abs.*, 1928, 22, 670.

## Chapter 29

### Urea Resins

#### III. Coating Compositions

Considering the preparation of lacquers from urea resins, it should be borne in mind that during the earliest stages of the urea-formaldehyde condensation the products are soluble in water or the formalin solution employed. The reaction product is at that stage, therefore, a hydrophilic colloid. On further condensation, however, the hydrophile becomes a hydrophobe and hence is insoluble in water.

For a number of purposes, urea resins may be used in the hydrophile stage, i.e., while still soluble in water, and, applied in this way, an inexpensive vehicle for the distribution of the condensation material is at hand. Water-soluble products are not desired, however, in a considerable number of applications where resins are employed, and the aim has been to produce resins which are soluble in organic solvents. This has been done, but, unfortunately, most of the effective solvents (such as the chlorohydrins) are costly.<sup>1</sup>

Another difficulty presenting itself is the tendency for urea resins in a lower stage of condensation to become converted gradually and spontaneously to a more highly condensed substance, so that a product which at one time is soluble in a given medium will later be found insoluble. Since the condensation of urea resins is usually accompanied by the liberation of small proportions of water, there is a tendency for the coatings to disintegrate long after they have dried. This may lead to the formation of fissures and to the disfigurement of the surface. Coatings which initially are bright and glossy may become dull and lusterless by the action of atmospheric moisture, if the stage of condensation of the material in the coating as initially applied is unduly low.

To improve the solubility of well-condensed urea resins in organic solvents and also to prevent the progress of further condensation after application, one development of manufacture comprises reacting urea and formaldehyde in the presence of an alcohol, butanol being particularly recommended, with the object of having the alcohol unite in the resin and confer solubility and stability. The results in this direction have been very promising, and lacquer compositions prepared in this manner have actually been brought on the market. Solid resins which are soluble in alcoholic solvents also are available.

#### UREA RESIN COATINGS

Aqueous solutions of the primary condensation products of urea and formaldehyde are colorless and can be made in various concentrations and viscosities. They show the typical properties of sols of highly solvated, hydrophilic colloids and have been suggested for various uses, including water-varnishes, adhesives and binding, impregnating and stiffening agents.

<sup>1</sup> See *Synthetic and Applied Finishes*, 1933, 3, 79.

A neutral solution of such a condensate was suggested as a lacquer or varnish by Ellis.<sup>2</sup> The solution is prepared by allowing 20 parts by weight of urea to react with 54 parts of formalin in the presence of 0.4 part of sodium hydroxide dissolved in an equal weight of water. As reaction proceeds the mixture eventually becomes turbid, and further interaction is checked by adding acid until the solution is substantially neutral. Glycerol, casein, gelatin, Irish moss, algin or pigments may be added. Applied to a surface, the solution dries and forms a varnish.

Ripper,<sup>3</sup> among others (see Chapter 28), used controlled hydrogen-ion concentrations as a means of obtaining urea resins for lacquer production. Thus, 30 parts by weight of urea are mixed with 100 parts of neutral 30 per cent formalin and heated in a boiler fitted with a reflux condenser. After a short time, 5 parts of boric acid dissolved in a little water are added, and the refluxing is continued for 6-7 hours. On standing in the cold for several hours longer, two layers are found to separate, the upper one being removed. The gel forming the lower layer is washed repeatedly with water and then dissolved in a non-aqueous solvent (epichlorohydrin). Mixed with softening agents, this lacquer solution gives a coating which is said to be insensitive to the action of water.

By incorporating water-soluble alginates (sodium alginate) with water-soluble urea- or thiourea-formaldehyde resins and an accelerator (e.g., acid potassium sulphate), Lefebure<sup>4</sup> obtained products of use as varnish stains, distemper paints and as impregnating agents for fiber boards. A colored urea resin lacquer is used for coatings on electric light bulbs.<sup>5</sup> The resin and dyes are applied to the bulbs by dipping, and the coating is hardened by the normal heat of the lamp.

Insoluble urea-formaldehyde products may be made soluble by heating with an excess of formaldehyde under pressure at a temperature above 100°C.<sup>6</sup> A suspension of the powdered resin in water or organic liquids can be applied to surfaces as a coating composition which is then dried and hardened by heat and pressure.<sup>7</sup> Hofer and Schmid<sup>8</sup> suggested the use of urea- or thiourea-formaldehyde resins together with a pigment for the production of a light-fast colored glaze on cement or tiles. A urea-thiourea-formaldehyde condensation product containing ammonium nitrate as hardening agent is stated to provide a waterproof glaze. Sodium phosphate was added as an accelerator to a thin paste (formed by heating urea, paraform and water at 90°C.) by Keller and Taylor<sup>9</sup> preparatory to forming a urea-formaldehyde varnish. According to Stoll,<sup>10</sup> natural or artificial stone and pottery may be coated with urea-formaldehyde resins in conjunction with a phenol-formaldehyde product and pigments. A temperature of 130°C. can be employed for hardening such coatings.<sup>11</sup> Another coating composition for use on wood,

<sup>2</sup> Carleton Ellis, U. S. P. 1,536,881, May 5, 1925; *Chem. Abs.*, 1925, 19, 1956. U. S. P. 1,846,853, Feb. 23, 1932; *Chem. Abs.*, 1932, 26, 2609.

<sup>3</sup> K. Ripper, U. S. P. 1,734,693, Nov. 5, 1929, to F. Pollak; *Chem. Abs.*, 1930, 24, 476. British P. 213,567, 1924; *J.S.C.I.*, 1925, 44, 681B.

<sup>4</sup> V. Lefebure, British P. 336,328, 1931; *Brit. Chem. Abs. B*, 1933, 238.

<sup>5</sup> E. A. Bevan, British P. 349,160, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 579. French P. 712,751, 1931; *Chem. Abs.*, 1932, 26, 1741.

<sup>6</sup> A. Gams and G. Widmer, U. S. P. 1,879,248, July 31, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1928, 22, 3792. German P. 499,589, 1925; *Chem. Abs.*, 1930, 24, 4597. British P. 246,126, 1925; *Chem. Abs.*, 1927, 21, 479. British P. 246,127, 1926; *Brit. Chem. Abs. B*, 1927, 684. Canadian P. 281,326, 1928; *Chem. Abs.*, 1928, 22, 3270. German P. 487,308, 1925; *Chem. Abs.*, 1930, 24, 2256. French P. 609,108, 1926; *Brit. Chem. Abs. B*, 1927, 223.

<sup>7</sup> British P. 401,689, 1932, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs. B*, 1934, 157. French P. 737,818, 1932; *Chem. Abs.*, 1933, 27, 1773. Swiss P. 162,213, 1933; *Chem. Abs.*, 1934, 28, 591. A similar coating composition contains a urea-aldehyde condensation product suspended in a solution of a soluble condensate of the same type. A. Gams and W. Fisch, U. S. P. 1,998,539, Apr. 23, 1935, to Soc. anon. pour l'ind. chim. à Bâle.

<sup>8</sup> P. Hofer and A. Schmid, British P. 348,063, 1929; *Chem. Abs.*, 1932, 26, 2880. French P. 689,173, 1930; *Chem. Abs.*, 1931, 25, 1109. German P. 601,275, 1934; *Chem. Abs.*, 1934, 28, 7465.

<sup>9</sup> A. V. Keller and J. Taylor, British P. 345,845, 1930, addn. to 331,428; *Brit. Chem. Abs. B*, 1931, 597.

<sup>10</sup> K. Stoll, British P. 282,786, 1926; *Chem. Abs.*, 1928, 22, 3971.

<sup>11</sup> German P. 550,319, 1928, to Mathys & Schaaf; *Chem. Abs.*, 1932, 26, 4151.

metals and cement consists of finely divided casein, urea, hexamethylenetetramine, lime and pigments.<sup>12</sup>

Dissolved intermediate condensates of the urea-formaldehyde reaction may be mixed with colloidal or semicolloidal substances obtained by the polymerization of unsaturated compounds of the type of vinyl esters, acrolein and itaconic acid. When modified by such additions, the resin is reported to be applicable to the manufacture of varnishes, films, artificial silk and molded articles.<sup>13</sup>

Natural resins can be blended with urea-formaldehyde-salicylic acid lacquers, according to Belfit.<sup>14</sup> The resins are first dissolved in a solvent, the nature of which is determined by the kind of resin concerned. Denatured alcohol can be used for shellac, and a mixture of denatured alcohol and butyl acetate serves as a solvent for mastic. Among the natural substances that may be employed are



*Courtesy Unyte Corporation*

FIG. 105.—Part of Control Laboratory in a Plant Manufacturing Urea Resin Molding Compositions.

kauri, sandarac, guaiac, dammar, camphor, Zanzibar, elemi, rosin and ester gum. These lacquers can be applied to metals (e.g., brass or gold).

A resin from thiourea, or from a mixture of thiourea and urea, and formaldehyde mixed with a hardening agent, e.g., a pasty mixture of paraformaldehyde and formaldehyde solution, is used with a solvent (ethyl lactate, ethylene glycol or the ethyl ether of ethylene glycol) to form a varnish.<sup>15</sup> Bender<sup>16</sup> found that a urea- or thiourea-formaldehyde resin in the initial stage of its condensation and dissolved in a high-boiling solvent could be advanced toward a more highly condensed (infusible) stage by heating. An infusible resin is obtained thus as a colloidal suspension that can be directly applied as a varnish. A varnish yielding flexible films and prepared by the addition of a plasticizer (butyl phthalate) to a urea-aldehyde resin was described by Turkington.<sup>17</sup> According to Bender<sup>18</sup> such a plasticized resin gives a firmly adherent coating with a glossy surface resistant to

<sup>12</sup> J. Eisenstein, U. S. P. 1,352,706, Apr. 5, 1932, to Chicago Paint Co.; *Chem. Abs.*, 1932, 26, 3125.

<sup>13</sup> British P. 309,487, 1928, to Kunstharzfabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1930, 24, 740. French P. 662,627 and 662,628, 1928; *Chem. Abs.*, 1930, 24, 475.

<sup>14</sup> R. W. Belfit, U. S. P. 1,998,755, Feb. 21, 1933, to Scovill Mfg. Co.; *Chem. Abs.*, 1933, 27, 2831.

<sup>15</sup> British P. 357,140, 1930, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 4720.

<sup>16</sup> H. L. Bender, British P. 349,599, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 729.

<sup>17</sup> V. H. Turkington, U. S. P. 1,695,566, Dec. 18, 1928, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 1000.

<sup>18</sup> H. L. Bender, British P. 355,318, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 1006.



moisture and heat. If the coating is applied to a viscose base, a product of high dielectric strength is obtained. Another method of forming a varnish is that of condensing thiourea (with or without additions of urea) and anhydrous formaldehyde in the presence of a monoalkyl ether of ethylene glycol and an alkyl lactate.<sup>19</sup> The proportions of the components are chosen so as to give a potentially reactive resin.

Christensen<sup>20</sup> described a composition for use as a varnish, sizing or paint, prepared by mixing "leather gum" and shellac with urea and aldol, acetaldehyde or paraldehyde. To prepare the "leather gum," leather scrap is treated for 6-24 hours with a 0.5-2 per cent solution of hydrochloric acid and removed to an open vessel containing water where it is boiled for 0.5-3 hours. The leather, now consisting almost entirely of fibrous protein material, becomes disintegrated and settles in the form of a heavy brown gum which is dried, and ground.

The surface of metals or other materials may be coated with lacquers prepared from urea resins and varying proportions of silicon or an acid-proof, heavy-metal silicide.<sup>21</sup> A basic, phenol-formaldehyde coating is usually first applied, and the thick covering layer is hardened.

#### FILM-HARDENING AGENTS

Belfit<sup>22</sup> investigated a group of compounds, including salicylic acid, gallic acid and hydroxynaphthoic acids, which when added to the resin solution increase the resistance of the final coating to solvents, sulphur compounds and other corrosive agents.

As an example, 400 g. of urea are dissolved in 2000 cc. of 40 per cent formaldehyde solution, and the mixture is heated on a steam bath until 40-60 per cent by weight has been evaporated. Water is then added to increase the weight to 75 per cent of its initial value. The solution is filtered to remove insoluble matter, and to 81 cc. of the solution are added 50 cc. of denatured alcohol, 42 cc. of butyl alcohol, 7 cc. of ethyl lactate and 5 g. of salicylic acid. The solvents in such a lacquer may be evaporated off in the air or by baking at 100°C. for a short period. The final hardening of the film is accomplished by heating at 130-135°C. for about 20 minutes. After hardening the first film, a second coating may be applied, as the solvents of the lacquer will not dissolve the hardened film. A thin layer of this lacquer is said to resist the attacks of sulphur compounds, alcohol, air, moisture and salt spray.

Various other ingredients may be incorporated in this type of lacquer. Thus, castor oil (in an amount equal to 2.5 per cent of the total proportion of solids present) serves as a plasticizer, increasing the pliability of the film and rendering it more impervious to liquids. One part of a lacquer consisting of 81 cc. of a urea resin solution, 50 cc. of denatured alcohol, 42 cc. of butyl alcohol, 7 cc. of ethyl lactate and 20 g. of salicylic acid may be admixed with 2 parts of a cellulose lacquer. The resulting composition is applied by spraying or dipping and is hardened by baking at 135°C.

The application of film-hardening agents (such as salicylic acid) may be extended to thiourea resins and to resins containing urea derivatives such as benzoyl-urea, acetylurea, cyanamide and guanidine.<sup>23</sup> Such modified urea-aldehyde resins lend themselves to the production of various types of lacquer compositions which are intended for protecting the surfaces of non-ferrous metals, including silver, nickel, copper, brass, aluminum and various alloys.

<sup>19</sup> British P. 358,898, 1930, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 4969 French P. 695,588, 1930. *Chem. Abs.*, 1931, 25, 2866

<sup>20</sup> P. C. Christensen, U. S. P. 1,901,145, March 14, 1933; *Chem. Abs.*, 1933, 27, 3094.

<sup>21</sup> G. Kraenzlein and R. K. Müller, U. S. P. 1,873,945, Aug. 23, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 6164. British P. 276,047, 1931; *Brit. Chem. Abs. B.*, 1932, 902.

<sup>22</sup> R. W. Belfit, U. S. P. 1,898,709, Feb. 21, 1933, to Scovill Mfg. Co.; *Chem. Abs.*, 1933, 27, 2831. British P. 292,912, 1927; *Chem. Abs.*, 1929, 23, 1517. French P. 659,327, 1928; *Chem. Abs.*, 1929, 23, 5339. Canadian P. 304,616, 1930; *Chem. Abs.*, 1930, 24, 6041.

<sup>23</sup> R. W. Belfit, U. S. P. 1,898,754 and 1,898,755, Feb. 21, 1933, to Scovill Mfg. Co.; *Chem. Abs.*, 1933, 27, 2831. Canadian P. 304,615, 1930; *Chem. Abs.*, 1930, 24, 6042.

Clear films, according to Belfit, are obtained by blending Bakelite lacquers with urea resin lacquers. A blended lacquer of this type may be composed of 7.5 gallons of Cellosolve (glycol monoethyl ether) containing 10 ounces of nitrocellulose per gallon, 14 gallons of denatured alcohol, 10 gallons of butyl alcohol, 10 gallons of ethyl lactate, 7.5 gallons of urea-formaldehyde-salicylic acid lacquer and 1 gallon of Bakelite lacquer.

Films of urea resins can be rapidly hardened by treatment with gaseous sulphur dioxide or solutions of the latter.<sup>24</sup> Aqueous solutions of sulphur dioxide frequently lead to surface opacity, but this may be overcome by using non-aqueous solutions or the gas itself. As an example, 6 kg. of urea, 200 g. of monosodium phosphate and 50 g. of disodium phosphate are dissolved in 5 l. of water and heated. The solution is slowly added to 18.75 kg. of a 32 per cent formaldehyde solution; and, after evaporation, the viscous condensation product is poured onto a smooth plate and exposed to an atmosphere of sulphur dioxide. After some minutes a hard superficial layer, which is no longer adhesive, has been formed. Other volatile acids or acid anhydrides can be employed.<sup>25</sup> The hardening effect varies with the kind and concentration of acid agent used.

#### UREA RESINS WITH NITROCELLULOSE

Urea-aldehyde condensation products have been employed in nitrocellulose lacquer compositions.<sup>26</sup> Some of their general properties<sup>27</sup> in this connection are illustrated by the "Plastopals,"<sup>28</sup> which are urea resins made in the presence of organic solvents. These substances are neutral, very pale in color and are light-fast.<sup>29</sup> They are soluble in alcohols, in glycol ethers (methyl, ethyl or butyl glycol), in cyclohexanone, diacetone alcohol and in mixed ester solvents. The Plastopals are insoluble in pure esters, ether esters, aliphatic ketones and aromatic hydrocarbons. They can be mixed with both ester-soluble and alcohol-soluble collodion cottons. In admixture with nitrocellulose, additions of castor oil may be made to the resins.

On heating for long periods the Plastopals become insoluble. Resins of this type incorporated with nitrocellulose are made insoluble more readily, being hardened in 24-48 hours at temperatures greater than 60°C. or in some weeks at room-temperature. The films obtained from such resins are slightly affected by water; but if nitrocellulose is a part of the composition, the coatings show good weather resistance. These products are very similar in many of their properties to ordinary shellac, although they are superior in their fastness to light, possess a more nearly water-white color and are completely homogeneous. They are useful in nitrocellulose lacquers containing alcohol as the main solvent and as a component of all types of wood lacquers. In contrast to the much-used spirit varnish resins, the urea resins give polishing lacquers that do not smear on rubbing with media containing mineral oil.

Resins of this general type may be prepared by the condensation of urea and formaldehyde in ethylene chlorohydrin. To 50 parts of a 50 per cent solution of the urea condensate in ethylene chlorohydrin is added a solution containing 3 parts of acetyl cellulose and 1 part of camphor in 50 parts of the same solvent.<sup>30</sup> When the solvent

<sup>24</sup> M. Luther, W. Pungs, R. Griessbach and C. Heuck, U. S. P. 1,794,084, Feb. 24, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2253

<sup>25</sup> See Chapter 27.

<sup>26</sup> B. N. Lougovoy, U. S. P. 1,922,890, Aug. 15, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 5159. U. S. P. 1,756,251, Apr. 29, 1930; *Chem. Abs.*, 1930, 24, 3122.

<sup>27</sup> For a review of the use of urea resins in nitrocellulose plastics, see H. Schmidt, *Nitrocellulose*, 1931, 2, 129; *Chem. Abs.*, 1931, 25, 4722

<sup>28</sup> The Plastopals are manufactured by the I. G. Farbenind. A.-G.

<sup>29</sup> See *Chem. Age (London)*, 1932, 26, 491. See also Carleton Ellis, *Ind. Eng. Chem.*, 1933, 25, 125

<sup>30</sup> H. Ramstetter and H. Krzikalla, German P. 404,024, to Badische Anilin- & Soda-Fabr. W. Pungs and K. Eisenmann, German P. 490,012, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24,

is evaporated from this lacquer, a clear film remains. A lacquer can be prepared by dissolving 5 parts of cellulose nitrate in 50 parts of a 30 per cent solution of a urea-formaldehyde resin in glycol monoacetate. The diethers of ethylene glycol are also used as solvents in these preparations.<sup>41</sup>

Using alcohols as solvents, condensation under mild conditions leads to the formation and separation of crystalline compounds, more highly condensed than dimethylolurea, as has already been discussed (see Chapter 26).<sup>42</sup> These substances may be subjected to further condensation in non-aqueous solution, either by fusion or by heating under pressure in alcoholic solution, in the absence of condensing agents, to make a lacquer.

Resins of similar type are prepared also from dimethylolurea, by suspending the substance in its own weight of methanol and boiling for 5-10 minutes with about 0.5 per cent of 1 *N* alcoholic hydrochloric acid. The mix is neutralized and filtered, and a crystalline product separates in colorless needles melting at 100-102°C. If 148 parts of this substance be heated with 175 parts of absolute methanol for half an hour at 80°C. under pressure, with an addition of 5 parts of sodium dihydrogen phosphate, condensation proceeds further. The mixture is neutralized with lime and filtered, yielding a lacquer containing 35-40 per cent of the condensation product.

The substances obtained by condensation in alcoholic solution are precipitated<sup>43</sup> by the addition of hydrocarbons, ethers (e.g., dioxane, anisole or glycol dialkyl ethers) and other non-hydroxylic compounds. The precipitated condensation product is freed from adhering solvents by washing with volatile inert liquids of the types named. The dried, powdered products are soluble in many hydroxylic solvents, in aldehydes and ketones (cyclohexanone) or in ester solvents, e.g., butyl acetate. Substances produced by condensation in the lower alcohols (ethanol or glycol) are somewhat sensitive to water, whereas the products from reaction mixtures of higher monohydric alcohols, especially amyl and benzyl alcohols, are practically unaffected by water, but are not readily freed from the high-boiling solvent. If, however, the washed condensation product, e.g., that from amyl alcohol, is dissolved in a volatile solvent (glycol monomethyl ether), there is obtained a water-resistant lacquer which does not retain the original, non-volatile solvent.

As an example of the application of the process to lacquer preparations, 50 parts of a 40 per cent solution of a condensation product of dimethylolthiourea in benzyl alcohol are stirred with 500 parts of ether. The precipitated solid is agitated several times with ether, filtered and dried *in vacuo* at 50°C. The powdered product may then be dissolved in an equal weight of glycol monomethyl ether at 80°C., and diluted with ethanol to form a lacquer which gives clear water-resistant coatings. Cellulose esters and softening agents may be incorporated. By heating 360 parts of dimethylolurea suspended in 500 parts of dioxane to 85°C. in the presence of 4 parts of oxalic acid, a higher condensation product is obtained.<sup>44</sup>

Lauter<sup>45</sup> concluded that the waterproof properties and the flexibility of urea-formaldehyde resins would be enhanced by carrying out the condensation in the presence of glycerol or other polyhydric alcohols. Not more than 1.2 mols of glycerol, according to Lauter, should be added per mol of urea, with one additional molar proportion of formaldehyde for each mol of glycerol.

2256. British P. 260,253, 1926; *Brit. Chem. Abs. B*, 1928, 237. French P. 641,420, 1926; *Chem. Abs.*, 1929, 23, 1227.

<sup>41</sup> British P. 256,229, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1927, 21, 2985.

<sup>42</sup> M. Luther and C. Heuck, U. S. P. 1,899,245, Jan. 15, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 1294. German P. 535,438, 1926; *Chem. Abs.*, 1932, 26, 1077. British P. 266,752, 1926; *Chem. Abs.*, 1928, 22, 849. British P. 296,361, 1927; *Chem. Abs.*, 1929, 23, 2540.

<sup>43</sup> W. Pungs, K. Eisenmann and J. Kuchenbuch, U. S. P. 1,836,553, Dec. 15, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1461. German P. 536,738, 1928; *Chem. Abs.*, 1932, 26, 1403. British P. 327,673, 1928; *Chem. Abs.*, 1930, 24, 5118. French P. 675,075, 1929; *Chem. Abs.*, 1930, 24, 2905.

<sup>44</sup> This material, after washing and drying, may be molded, forming transparent, homogeneous masses.

<sup>45</sup> F. Lauter, U. S. P. 1,633,337, June 21, 1927, to Röhm & Haas Co.; *Chem. Abs.*, 1927, 21, 2568. British P. 256,248, 1926; *Brit. Chem. Abs. B*, 1928, 165.

Lacquers<sup>36</sup> may be obtained by carrying out the condensation in the presence of halogenated aromatic alcohols or of glycols partially esterified with halogenated aryl groups, but containing unsubstituted hydroxyl radicals. Appropriate solvents are *o*-chlorobenzyl alcohol, glycol monobromophenyl ether and glycol bromosalicylate, using acetic acid or oxalic acid as condensing agents.

The condensation of urea (or thiourea) and formaldehyde or its polymers at a temperature of 100-160°C. and in the presence of a hydroxylated solvent (butanol or isobutanol) as discussed previously, furnishes substances that can be used with cellulose esters or ethers and oils in the production of lacquers.<sup>37</sup>

Thus, Neubauer<sup>38</sup> described the preparation of lacquers and films by dissolving 10 parts of a 50 per cent methyl alcohol solution of such a condensation product of urea and formaldehyde in 40 parts of a 20 per cent nitrocellulose solution and adding 20 parts of hexyl acetate together with 20 parts of benzene. The clear, viscous solution obtained furnishes smooth and glossy coatings when sprayed on leather, glass, paper, wood and textiles. Replacing the hexyl acetate and benzene with 20 parts of ethylene glycol monoethyl ether, 24 parts of cyclohexanol, 8 parts of butyl alcohol and 8 parts of propyl alcohol, a lacquer which forms smooth, supple and firmly adherent coatings is compounded.

Pungs and Eisenmann<sup>39</sup> employed a urea resin condensed in butyl alcohol for varnishes together with nitrocellulose and a drying oil varnish. As an example, 18 parts of a 43 per cent solution of a urea resin in isobutyl alcohol are mixed with a solution of 3 parts of nitrocellulose and 6 parts of an oil varnish consisting of 66 parts of melted Congo copal, 33 parts of boiled linseed oil and 1 part of cobalt resinate all dissolved in 10 parts of butyl acetate, 25 parts of ethyl alcohol and 35 parts of toluene. To this composition, 6 parts of an oily fraction boiling at 150-190°C. obtained by the catalytic hydrogenation of oxides of carbon are added. The resulting lacquer gives clear, hard films.

Vegetable or animal oils, including linseed oil, castor oil and cod-liver oil, that have been pretreated with oxidizing gases at 140-180°C. can be incorporated with urea-formaldehyde resins and nitrocellulose to form lacquers.<sup>40</sup> The oxidation conditions must be controlled to insure the formation of a viscous oil and not a jelly. The odor of the oxidation product is removed, or at least improved, by treatment with hydrogen and a hydrogenating catalyst, care being taken to keep the products from solidifying. The hydrogenation of the oil may be performed before the oxidation treatment. The added oils and the use of relatively large proportions of nitrocellulose improve the water-resistance, flexibility and the adhesive properties of the lacquer coating.

To illustrate the preparation, 140 parts of a 43 per cent isobutyl alcohol solution of the condensation product are mixed with a solution of 60 parts of nitrocellulose and 45 parts of shark oil (pretreated with oxidizing gases) in 100 parts of butyl acetate, 200 parts of ethyl lactate, 300 parts of ethyl alcohol and 300 parts of toluene. The resulting composition is a clear, transparent lacquer. Solid urea-formaldehyde condensation products may be treated with organic solvents to separate the solid, insoluble part from the viscous, soluble portion.<sup>40a</sup> The solid, brittle component is used for

<sup>36</sup> J. Kuchenbuch and K. Eisenmann, German P. 516,995, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1967. British P. 338,937, 1929; *Chem. Abs.*, 1931, 25, 2581. French P. 38,157, 1930, addn. to 641,420; *Chem. Abs.*, 1931, 25, 5555.

<sup>37</sup> British P. 359,147, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4970. British P. 344,626, 1930; *Chem. Abs.*, 1931, 25, 4725. French P. 711,788, 1931; *Chem. Abs.*, 1932, 26, 2073.

<sup>38</sup> C. Neubauer, U. S. P. 1,902,337, Mar. 21, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3301. German P. 527,403, 1925; *Chem. Abs.*, 1931, 25, 4725. British P. 262,818, 1926; *Brit. Chem. Abs. B.*, 1927, 947.

<sup>39</sup> W. Pungs and K. Eisenmann, U. S. P. 1,982,881, Dec. 4, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 627. British P. 322,780, 1928, addn. to 301,133; *Brit. Chem. Abs. B.*, 1930, 338. French P. 671,158, 1929; *Chem. Abs.*, 1930, 24, 1996.

<sup>40</sup> W. Pungs and K. Eisenmann, U. S. P. 1,904,528 and 1,904,529, Apr. 18, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3623. Canadian P. 284,970, 1928; *Chem. Abs.*, 1929, 23, 999. French P. 36,547, 1929, addn. to 653,026; *Chem. Abs.*, 1930, 24, 6040. French P. 653,026, 1928; *Chem. Abs.*, 1929, 23, 3321. British P. 287,116, 1926; *Brit. Chem. Abs. B.*, 1928, 531. British P. 301,133, 1928; *Brit. Chem. Abs. B.*, 1929, 104.

<sup>40a</sup> W. Pungs, K. Eisenmann and J. Kuchenbuch, German P. 522,891, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3782.

lacquers and artificial masses, and the viscous part is used as glue or as a softener for cellulose.

Lougovoy<sup>41</sup> also prepared lacquers by mixing urea-formaldehyde condensates with nitrocellulose. Urea (10 parts) and formalin (60 parts) are refluxed in an approximately neutral medium for 15-60 minutes giving a syrupy product which is diluted with an equal volume of acetone. Acetone will mix in the cold with many urea-formaldehyde syrups. Alcohol, however, is not as miscible and is best added to the hot condensate. Furfural and also phenol can be employed as solvents for the resin syrup. To 100 parts of the acetone solution of the urea condensate 5-50 parts of nitrocellulose may be added. The nitrocellulose-urea solutions give light-colored coatings when applied to wood or other surfaces.

Electrical insulating materials for use as coatings are obtained by incorporating castor oil, nitrocellulose and rosin with a urea-formaldehyde resin.<sup>42</sup> For example, 33 parts of a 46 per cent solution of urea resin in butyl alcohol are mixed with a solution of 15 parts of nitrocellulose, 30 parts of blown castor oil and 6 parts of rosin in 25 parts of butyl acetate, 75 parts of ethyl alcohol and 75 parts of toluene. These coatings are adherent, elastic and durable after drying for 8 hours at 75°C. They resist many mineral acids and are unattacked by transformer oils at high temperatures.

Only polymerization products of diolefins (e.g., butadiene), polymerized without the aid of alkali metals, have also been suggested for incorporation with cellulose esters or ethers and urea-formaldehyde resins in the manufacture of coating compositions.<sup>43</sup>

Eisenmann and Kollman,<sup>44</sup> developed a method of producing lacquers from the condensation products of urea and related compounds with formaldehyde by heating these products suspended in an anhydrous solvent with a substance capable of taking up water. Thus, 150 parts of dimethylolurea and 50 parts of dimethylolthiourea are suspended in 250 parts of benzyl alcohol. While stirring, the mixture is heated to 110°C. with 36 parts of anhydrous calcium nitrate and kept at this temperature for 2 hours. After removing the calcium nitrate a clear solution is obtained which may be mixed with nitrocellulose, forming a coating with a high luster. The condensation may also be carried out with hydrochloric acid in hot ethyl alcohol solution.<sup>45</sup> Sodium acetate is added and the alcohol evaporated, giving a resin which hardens to a transparent material on heating. Using isobutyl alcohol as a medium, Pungs and Eisenmann<sup>46</sup> heated 200 parts of dimethylolurea in an autoclave to 135°C. and at a pressure of 8 atmospheres. The clear solution obtained by cooling gave a solid condensation product after steam distillation.

The condensation of dimethylolurea (or of dimethylolurea ethers) to vitreous masses or lacquers may conveniently be effected by passing a buffered urea-formaldehyde solution continuously through a system of tubes at 100°C.<sup>47</sup> discharging into a vacuum drier. If, instead of an aqueous vehicle, alcoholic media (e.g., isobutanol) be employed, the acidic buffering salts (usually primary and secondary sodium phosphate) are neutralized with sodium carbonate. The solutions are clarified in a centrifuge and may then be used as lacquers.

<sup>41</sup> B. N. Lougovoy, U. S. P. 1,922,690, Aug. 15, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 5159. See also U. S. P. 1,756,251, Apr. 29, 1930; *Chem. Abs.*, 1930, 24, 3122.

<sup>42</sup> French P. 674,611, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2816.

<sup>43</sup> British P. 359,944, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 118.

<sup>44</sup> K. Eisenmann and T. Kollman, U. S. P. 1,948,343, Feb. 20, 1934, to Unyte Corp.; *Chem. Abs.*, 1934, 28, 2927. German P. 552,264, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4425.

<sup>45</sup> British P. 359,944, 1930; *Chem. Abs.*, 1932, 26, 4970. French P. 712,069, 1931; *Chem. Abs.*, 1932, 26, 2073.

<sup>46</sup> British P. 361,029, 1925, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1928, 532. C. Heuck, German P. 495,790, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 3615.

<sup>47</sup> W. Pungs and K. Eisenmann, U. S. P. 1,967,685, July 24, 1934, to Unyte Corp.; *Chem. Abs.*, 1934, 28, 5941.

<sup>48</sup> M. Luther, U. S. P. 1,947,997, Feb. 20, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2927. British P. 306,875, 1927; *Chem. Abs.*, 1929, 23, 5197. French P. 651,035, 1928; *Chem. Abs.*, 1929, 23, 3315. British P. 320,915, 1928; *Chem. Abs.*, 1930, 24, 2623. C. Heuck and M. Luther, German P. 548,372, 1927; *Chem. Abs.*, 1932, 26, 4142.

Treatment of dimethylolurea with alkaline reagents (suspended or dissolved in phenolic solvents to absorb disengaged formaldehyde)<sup>48</sup> yields partially dehydrated products of higher molecular weight, which may then be resinified by condensation in hot acid solution.

Coating compositions for wood, natural or imitation leather, brickwork, asbestos, paper or textiles can be prepared by emulsifying solutions of cellulose esters, in water-insoluble organic solvents, with aqueous solutions of urea-formaldehyde resins, softening agents, other emulsifying or wetting agents, coloring materials and extending agents.<sup>49</sup> Threads or films made from mixtures of cellulose esters or ethers and urea resins are said to possess greater strength than the purely cellulosic material.<sup>50</sup> The condensation of toluene sulphonamide with formaldehyde and urea gives a product that may be mixed with cellulose compositions in the manufacture of films, filaments and coating compositions.<sup>51</sup>

<sup>48</sup> British P. 301,696, 1928, addn. to British P. 261,020, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 138.

<sup>49</sup> British P. 334,567, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1108

<sup>50</sup> British P. 294,485, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 2032

<sup>51</sup> W. H. Moss and B. B. White, British P. 317,456, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 2317. British P. 344,413, 1928; *Chem. Abs.*, 1931, 25, 4725. See also Chapter 34.

## Chapter 30

### Urea Resins

#### IV. Miscellaneous Uses

The applications of urea resins in coating compositions, in molding powders and in attempts to prepare organic glass have been discussed,<sup>1</sup> but there remain various special and miscellaneous uses which will be treated in this chapter. Among these diverse adaptations are the treatment of textiles with urea resins for the purpose of conferring crease-resistant properties, the production of adhesives, the impregnation of wood, paper and other cellulosic materials, the manufacture of safety glass, and other applications.

##### TREATMENT OF TEXTILE MATERIALS

The urea-formaldehyde resins have found considerable application in the treatment of textile materials to render them crease-proof.<sup>2</sup> Clayton,<sup>3</sup> in discussing the use of synthetic resins for conferring anti-crease properties on textiles, drew attention to the non-creasing attributes of good quality woolen fabrics. Cotton goods, however, crumple readily since the cotton fibers are relatively plastic. Linen and artificial silk behave like cotton in this respect. After treatment with synthetic resins, woven and knitted cellulose fabrics approach wool or silk in their resistance to and recovery from creasing, without losing their draping qualities or handling simplicity. Similarly treated regenerated cellulose possesses an increased dry strength and a greatly increased wet strength. The weight of the treated material is increased by an average of 15 per cent. The anti-crease process reduces the textile's tendency to slip and to shrink (when laundered). The extensibility of artificial silk is also reduced; and, thus, the many forms of distortion to which this material is especially susceptible are less likely to occur.

The general method of processing the fabrics is about as follows.<sup>4</sup> The fibers of cotton or rayon material are treated with alkali until the cellulose is considerably swollen, the alkali is washed out, and the wet material is then impregnated with the resin components. Phenol-formaldehyde resins, as well as those from urea and formaldehyde, can be used in treating the cloth. If urea resin is employed, 1 part of urea and 2 parts of a 40 per cent formaldehyde solution are mixed, made slightly alkaline with hexamethylenetetramine or sodium hydroxide, boiled under reflux for 3-5 minutes and cooled quickly. The mixture (3 parts) is diluted with 1 part of water, and 0.5-0.75 per cent of acetic acid or an equivalent amount of any weak acid is added.

The squeezed, damp mercerized cloth is run, with repeated nippings between rollers,

<sup>1</sup> See Chapters 27, 28 and 29.

<sup>2</sup> See J. F. Warner, *Rayon*, 1933, 14 (9), 19; *Chem. Abs.*, 1934, 28, 4241. H. Roche, *Silk J.*, 1933, 10 (112), 22; *Chem. Abs.*, 1934, 28, 4241. See also *Synthetic and Applied Finishes*, 1933, 3, 85.

<sup>3</sup> E. Clayton, *J. Soc. Dyers Colourists*, 1932, 48, 295; *Chem. Abs.*, 1933, 27, 421. See also H. Hart, *Kunstseide*, 1932, 14, 409; *Chem. Abs.*, 1933, 27, 2818.

<sup>4</sup> R. P. Foulds, J. T. Marsh and F. C. Wood, U. S. P. 1,734,516, Nov. 5, 1929, to Tootal Broadhurst Lee Co., Ltd.; *Chem. Abs.*, 1930, 24, 511. R. P. Foulds, J. T. Marsh, F. C. Wood, H. Boffey and J. Tankard, British P. 291,473, 1926; *Chem. Abs.*, 1929, 23, 1289 French P. 657,348, 1927; *Chem. Abs.*, 1929, 23, 4353. German P. 499,818, 1927; *Chem. Abs.*, 1930, 24, 4643.

through the resin mixture. The fabric is then dried at a low temperature, and the resin is made insoluble by heating at 180°C. The acetic acid acts as a catalyst for the resin condensation which occurs on the fibers. It is important that an acid and not an alkali be used as catalyst at this stage; for with an alkaline reagent, the non-crush effect becomes less resistant to washing. When phenol-formaldehyde resins are substituted for those from urea and formaldehyde,<sup>6</sup> acid or alkaline catalysts can be employed in the condensation. Too much resin must not be added to the fabric since this would cause stiffness and actually promote the creasability of the material.

In order to render cotton or rayon fabrics less susceptible to creasing and wrinkling while still preserving their suppleness, Zänker<sup>6</sup> applied a water-soluble urea-formaldehyde resin together with a metallic salt (acetates or other salts of zinc, aluminum, zirconium, tin or titanium). After impregnation in a solution of these components, the fiber is heated, resulting in the formation of an insoluble resin and a water-soluble inorganic compound. The proportions of resin and metallic compound used are too small to cause appreciable stiffness.

Horsfall and Lawrie<sup>7</sup> found that urea-formaldehyde resins greatly reduce or prevent the deterioration of animal fibers and fur by acid or alkaline media. Such protective action is needed in wool scouring and the dyeing of wool or silk with vat colors. Thus, unscoured wool is treated for 0.5-0.75 hour at 45-50°C. in a bath containing 10 per cent by weight of sodium carbonate (calculated on the weight of the wool) and 5 per cent of dimethylolurea. The wool is sufficiently scoured in this manner without suffering damage (e.g., tendering or loss of elasticity) from the injurious action of the alkali.

Cotton, silk, artificial silk or fabrics made from such materials may be treated with aqueous thiourea-formaldehyde resin solutions, and the condensation of the resin completed on the fiber by an acid condensing agent (oxalic acid).<sup>8</sup> The final condensation is carried out at 120-140°C., whereby the resin is made insoluble and a stiffening effect is obtained in the fabric. The impregnating solution also contains fillers including starch, gums and China clay. The quality of cloth and thread is improved, according to Syôji,<sup>9</sup> by similar means. The material is treated at 80°C. with a water-soluble urea-formaldehyde condensation product and dilute acid (0.3 per cent sulphuric acid) is applied; after which the textile is washed with water and dried.

Pollak<sup>10</sup> employed urea-formaldehyde resins for stiffening felt hats and paper. The raw hats are stretched on wooden blocks or models and impregnated with a solution containing from 5-10 per cent of the resin. Then they are treated with dry steam, until the odor of formaldehyde has decreased considerably, and are smoothed with a hot iron. Writing papers are similarly stiffened with a colorless and transparent coating.

Urea-formaldehyde resins, according to Heuck and Esselmann,<sup>11</sup> are able to reduce the swelling-capacity of hydrated cellulose, hence treatment with urea

<sup>6</sup> R. P. Foulds, J. T. Marsh and F. C. Wood, British P. 291,474, 1926, to Tootal Broadhurst Lee Co., Ltd.; *Chem. Abs.*, 1929, 23, 1288. R. P. Foulds and J. T. Marsh, British P. 304,900, 1928; *Chem. Abs.*, 1929, 23, 4832.

<sup>7</sup> W. Zänker, U. S. P. 1,925,914, Sept. 5, 1933, to Heberlein Patent Corp.; *Chem. Abs.*, 1933, 27 5553. British P. 413,328, 1933, to Heberlein & Co. A.-G.; *Brit. Chem. Abs. B*, 1934, 831.

<sup>8</sup> R. S. Horsfall and L. G. Lawrie, U. S. P. 1,693,926, Dec. 4, 1928, to Brit. Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1929, 23, 996. British P. 285,554, 1926; *Brit. Chem. Abs. B*, 1928, 363.

<sup>9</sup> E. C. Roseiter and W. C. Davis, U. S. P. 1,926,063, Sept. 12, 1933, to Synthetic Plastics, Co.; *Chem. Abs.*, 1933, 27, 5990. British P. 258,357, 1925, to Brit. Cyanides Co., Ltd.; *Chem. Abs.*, 1927, 21, 3135.

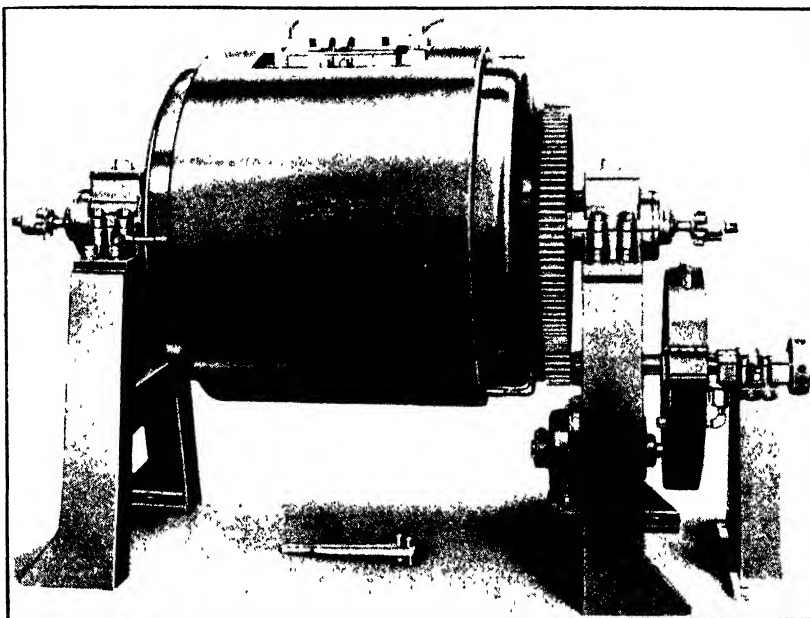
<sup>10</sup> I. Syôji, Japanese P. 100,072, 1933; *Chem. Abs.*, 1934, 28, 2547. A. L. Eidlin (Russian P. 81,616, 1933; *Chem. Abs.*, 1934, 28, 3258) also condensed urea and aldehydes on a fabric.

<sup>11</sup> F. Pollak, British P. 157,416, 1922; *J. S. C. I.*, 1922, 41, 459A.

<sup>12</sup> C. Heuck and P. Esselmann, U. S. P. 1,737,760, Dec. 3, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 960. German P. 537,036, 1927; *Chem. Abs.*, 1932, 26, 1118. O. Faust and P. Esselmann, German P. 535,234, 1926; *Chem. Abs.*, 1932, 26, 1118. British P. 278,684, 1927; *Brit. Chem. Abs. B*, 1929, 242. French P. 636,803, 1927. See also French P. 770,956, 1934, to Soc. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1935, 29, 941.



resins increases the strength of viscose in the wet state. Viscose is soaked in a solution containing 40 parts of dimethylolurea and 0.4 part of sodium phosphate in 1000 cc., and is then dried for 24 hours at 110-120°C. to convert the resin to the insoluble form. During the impregnation, a solvent miscible with water, a softener and a wetting agent may also be added to the bath. Natural or artificial textile fibers can be given an uncrushable finish by the use of urea-formaldehyde resins condensed with alkalies.<sup>12</sup>



*Courtesy Paul O. Abbé, Inc.*

FIG. 106.—Pebble Mill, Jacketed with Silent Chain and Motor Drive, Used for Grinding Urea Plastics.

Urea resins have been used with glass particles, metal or pearl dust, mica flakes, wool and cotton in producing ornamented materials.<sup>13</sup> Chaloupka<sup>14</sup> also described a method of ornamenting silk, gauze and other pliable fabrics with spaced, globular deposits of the hard, insoluble, final condensation product of urea and formaldehyde. The local effects produced by employing urea resins during the processing of the material are varied and numerous.<sup>15</sup>

Thus, if acetate silk is printed with a paste containing gum arabic and 5 per cent of dimethylolurea and steamed or hung in the air, damask effects are obtained, since the printed spots are dull on the glossy original ground of silk. Other effects are given by a paste prepared from 200 parts of smalt, 775 parts of aqueous (1:1) British gum (dextrin) and 25 parts of mono- or dimethylolurea. By printing a fabric with this paste and then treating with steam, dark-blue prints, fast to rubbing and washing, are obtained.

<sup>12</sup> French P. 766,829, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 7556.

<sup>13</sup> J. C. Vredenburg and F. A. H. Heynert, British P. 277,091, 1926, to British Bead Printers, Ltd.; *Chem. Abs.*, 1928, 22, 2446.

<sup>14</sup> J. Chaloupka, U. S. P. 1,657,067, Jan. 24, 1928; *Chem. Abs.*, 1928, 22, 1050.

<sup>15</sup> A. Schneevogt and A. Nowak, U. S. P. 1,871,087, Aug. 9, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5772. British P. 328,978, 1928; *Brit. Chem. Abs. B*, 1930, 763. French P. 678,510, 1929.

Heynert and Lucius<sup>16</sup> used a composition consisting of 15-60 per cent of cellulose esters or ethers together with 85-40 per cent of a syrupy condensation product from urea or thiourea and formaldehyde for the ornamentation of fabrics and yarns. Paper, linen or other cellulosic material which is to receive color or design may be impregnated with urea resins and then hot-pressed.<sup>17</sup>

Acid dyes, e.g., a dye obtained from 5-aminotoluene-2-sulphonic acid and  $\beta$ -naphthol, are converted into lakes in the presence of aqueous solutions of urea-formaldehyde resins.<sup>18</sup> Urea resins dissolved in chlorohydrins are used in conjunction with the usual printing media to render pigments and dyestuffs, applied to fabrics, fast to washing.<sup>19</sup> The affinity of textiles for dyes may be varied by a previous impregnation or printing with an aqueous solution of a urea-formaldehyde condensation product.<sup>20</sup> The condensate is rendered insoluble prior to the dyeing process.

### IMPREGNATION OF PAPER AND CELLULOSIC MATERIALS WITH UREA RESINS

Mention has already been made of the treatment of paper with a urea condensate. According to Atsuki and Matsuoka,<sup>21</sup> urea resins in general increase the dielectric strength of paper when used as an impregnant, although spruce sulphite paper impregnated with a urea resin exhibits a lower mechanical strength than the untreated substance. Paper resembling "glassine" is obtained by adding a gel prepared by treating a 2 per cent urea solution with formaldehyde and acetic acid to the pulp contained in the beater.<sup>22</sup>

Lionne<sup>23</sup> modified the impregnation method by first preparing a gum-like material through the interaction of 100 parts of urea, 50 parts of acetaldehyde, 50 parts of glycerol (plasticizer) and 10 parts of glacial acetic acid. The reaction is carried out in the cold, and 100 parts of the stock so obtained are treated with 150 parts of formaldehyde and 2-5 parts of ammonium sulphate. The resultant jelly, if allowed to stand, would change gradually into a hard resin, unsuited for incorporation with paper. Consequently, a "retarder" is introduced prior to the jelly-formation in order to reduce the tendency of the jelly to pass into the higher condensation stages. Lionne states that a mixture containing 100 parts of water and 2.5 parts of Karaya gum accomplishes this aim. In preparing the paper, the weight of jelly taken varies from 5-100 per cent of the weight of pulp, and the dispersion of the components is carried out in a beater. The paper is finally calendered (usually with heat) and then appears translucent and seemingly parchmentized. Simultaneously, the tensile strength and the chemical and electrical resistance are said to be improved. If the paper is hot-calendered, the resin is converted into its insoluble stage, reducing the flexibility of the product.

Urea resins are utilized as a means of insuring the permanence of designs or decorations on paper and fabrics. The paper is dipped in the resin (urea- or thiourea-formaldehyde) solution; and, on the application of heat and pressure (by passing through heated rollers), a smooth lustrous surface is obtained which can be washed without marring the surface.<sup>24</sup> The incorporation of finely comminuted fibers has been suggested as a means of preventing the formation of

<sup>16</sup> F. A. H. Heynert and F. Lucius, British P. 376,540, 1931; *Brit. Chem. Abs.* B, 1932, 932.

<sup>17</sup> British P. 375,791, 1931, to H. Römmler A.-G.; *Brit. Chem. Abs.* B, 1932, 902.

<sup>18</sup> British P. 359,643, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 427. French P. 717,606, 1931; *Chem. Abs.*, 1932, 26, 2875.

<sup>19</sup> H. Krikalla and A. Schneivoigt, German P. 433,152, 1924, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1927, 197. G. Schwen and C. Schöller, German P. 562,382, 1931; *Chem. Abs.*, 1933, 27, 853.

<sup>20</sup> G. Spencer, British P. 301,365, 1923, to Pollopas, Ltd.; *Brit. Chem. Abs.* B, 1929, 127. French P. 609,926, 1923; *Chem. Abs.*, 1930, 24, 1990.

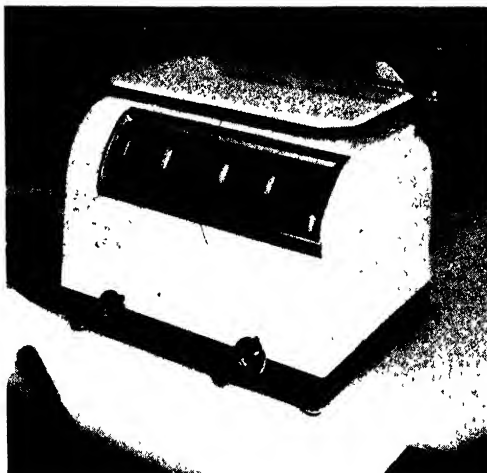
<sup>21</sup> K. Atsuki and K. Matsuoka, *J. Soc. Chem. Ind. Japan*, 1930, 335B; *Chem. Abs.*, 1931, 25, 4123.

<sup>22</sup> A. L. Clapp, U. S. P. 1,820,962, Sept. 1, 1931; *Chem. Abs.*, 1931, 25, 5991.

<sup>23</sup> E. Lionne, U. S. P. 1,847,778, Mar. 1, 1932; *Chem. Abs.*, 1932, 26, 2598.

<sup>24</sup> E. C. Rossiter and C. H. Cooper, British P. 246,886, 1924, to Brit. Cyanides Co., Ltd.; *Chem. Abs.*, 1927, 21, 495.

fine cracks within the surface.<sup>28</sup> In experiments carried out by Ellis<sup>29</sup> on the production of laminated paper with differently colored strata, a mixture of 1 part of acetone-formaldehyde resin with 3-4 parts of urea-formaldehyde resin is employed as an impregnant. A vari-colored effect is obtained by dyeing the paper with different colors or by treating the resin solutions with various pigments. A highly calendered, waterproof sulphite cellulose paper coated on both sides with a condensate formed from urea and formaldehyde and then hardened was used by Wickel<sup>30</sup> in the manufacture of drinking-straws. An additional method for the manufacture of transparent paper employs parchment paper which is treated with a urea-formaldehyde condensation product, dried, and heated to 120-150°C. to make it transparent.<sup>31</sup> Paper or other absorbent medium, impregnated with a resin from formaldehyde or furfural with phenol, cresol or urea, was used in the



Courtesy Plaskon Co.

FIG. 107.—A Scale Made of a Urea-Formaldehyde Resin.

construction of acoustic diaphragms.<sup>32</sup> Porous panels of cellulosic fibers can be impregnated with an alcoholic solution of a urea-formaldehyde condensation product which is later made insoluble by heating at 100°C.<sup>33</sup> Boards for building or fitting purposes can be formed by drying (with heat and pressure) sheets obtained from aqueous suspensions of wood fiber containing, in solution, urea, thiourea and an aldehyde.<sup>34</sup> A sound-record blank consists of a core of paper impregnated with urea resin and coated first with a nitrocellulose solution and then with one of cellulose acetate.<sup>35</sup>

Urea resins are produced as covering layers on various materials (e.g., asbestos plates, absorbent paper or printed material) by impregnating with a suspension

<sup>28</sup> J. D. Cochrane, Jr., U. S. P. 1,997,353, Apr. 9, 1935, to Formica Insulation Co.

<sup>29</sup> Carleton Ellis, Reissue 18,370 of U. S. P. 1,685,355, Mar. 1, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1932, 26, 2009.

<sup>30</sup> F. K. Wickel, U. S. P. 1,888,898, Nov. 22, 1932. British P. 376,200, 1931, to Wickel & Co. Kom.-Ges.; *Chem. Abs.*, 1933, 27, 3333.

<sup>31</sup> German P. 551,856, 1928, to Real. des brevets Francais Amouroux & Cie.; *Chem. Abs.*, 1932, 26, 4953. See also V. Bausch and K. Frenzel, U. S. P. 1,856,067, May 3, 1932; *Brit. Chem. Abs.* B, 1933, 265.

<sup>32</sup> British P. 316,203, 1928, to N.-V. Philips' Gloeilampenfabr.; *Chem. Abs.*, 1930, 24, 1711.

<sup>33</sup> French P. 45,311, 1934, addn. to 748,854, to Soc. Nobel franc.; *Chem. Abs.*, 1934, 28, 5206.

<sup>34</sup> British P. 407,161, 1934, to Aktiebolaget Mo och Domejo Wallboard Co.; *Chem. Abs.*, 1934, 28, 5205.

<sup>35</sup> S. Whyte, U. S. P. 1,997,398, Apr. 9, 1935, to Radio Corp. of America.

of the condensate, drying and hardening with heat and pressure.<sup>32</sup> The suspension consists not only of urea-formaldehyde condensate suspended in water or an organic solvent but also the solid resin swollen by the liquid phase. Fillers, pigments and plasticizers together with bronze powder or metal filings may be incorporated with the solid resin. Lahousse<sup>33</sup> prepared impregnated paper for the manufacture of electric condensers by using amido substances (including anilides, thioamides, urea, ureines, ureides, thiourea and sulphonamides) with resins, waxes and paraffin.

Combustible materials can be fireproofed by treatment with solutions or suspensions of fireproofing salts in urea-formaldehyde condensation products to which have been added pigments for the production of decorative effects.<sup>34</sup>

### NON-SHATTERING GLASS AND ADHESIVES

The quality of light-fastness which urea resins possess to a high degree has caused them to be suggested as adhesives in the production of safety glass.<sup>35</sup>

Davis<sup>36</sup> prepared a resin solution for use as an interlayer and adhesive in safety glass by first evaporating 10 parts of dicyanodiamide, 28 parts of thiourea, 22 parts of urea, 126 parts of 40 per cent formaldehyde and 1.4 parts of formic acid at 70°C. until the mixture corresponded to 134 parts by weight. Then, 10 parts of the prepared composition are shaken with 50 parts of acetone, and to 37 parts of the clear extract are added 6.1 parts of low-viscosity nitrocellulose dissolved in a mixed solvent containing 16.5 parts of acetone, 12 parts of alcohol, 18 parts of benzene, 1.8 parts of benzyl alcohol, 9 parts of mono-ethyl ether of ethylene glycol and 5 parts of butyl phthalate. The adhesive solution is painted or otherwise spread on one side of each of the glass sheets to be used and is allowed to dry for 2-10 minutes. A cellulose acetate sheet is applied as an interlayer between two such coated glass sheets, and the whole is subjected to a pressure of 500 lb. per square inch, heat being applied until the temperature reaches about 50°C.

This procedure with a number of modifications is the basis for several proposed methods of making nonshatterable glass. Various cellulose esters, ethers, plasticizers and dyes may be added,<sup>37</sup> and the hardening of the resin layer may be hastened by the addition of a hardening catalyst.<sup>38</sup> Voluinkin<sup>39</sup> used alcohol as the solvent for the urea resin, the alcohol being removed before pressing by drying at a temperature of about 100°C. Segond<sup>40</sup> prepared a product suggested for use in safety glass by condensing urea with formalin in the presence of a mixture containing dry zinc powder, sodium chloride, trioxymethylene and hexamethylenetetramine.

Ford and McCarroll<sup>41</sup> recommended uniting sheets of rough, translucent glass and interposed cellulosic sheets with compositions having the same refractive index as the glass. A composition achieving this result is composed of 50-55 per cent of cellulose nitrate, 20-25 per cent of urea-formaldehyde resin, 10-15 per cent of camphor and 10-15 per cent of tolyl phosphate. As an adhesive for the glass, Rossiter<sup>42</sup> used a mixture of about 30 per cent of urea resin and 70 per cent of gelatin. A dicyanodiamide-formaldehyde resin may be substituted for the urea resin, and the final adhesion after assembling the sheets is effected by compression at 80°C. These resins were

<sup>32</sup> British P. 401,589, 1933, to Soc. anon. pour l'ind. chim à Bâle; *Chem. Abs.*, 1934, 28, 2928.

<sup>33</sup> J. Lahousse, British P. 251,970, 1925; *Chem. Abs.*, 1927, 21, 1505.

<sup>34</sup> German P. 532,578, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 569. German P. 589,649, 1933; *Chem. Abs.*, 1934, 28, 2496. See also S. Tamura, Japanese P. 98,797, 1932; *Chem. Abs.*, 1933, 27, 5931.

<sup>35</sup> *Chem. Age (London)*, 1932, 27, 472. See also *Plastic Products*, 1934, 10, 131.

<sup>36</sup> W. C. Davis, U. S. P. 1,864,933, June 28, 1932; *Chem. Abs.*, 1932, 26, 4432.

<sup>37</sup> British P. 245,758, 1929, to Brit. Celanese, Ltd.; *Chem. Abs.*, 1932, 26, 574.

<sup>38</sup> E. Geisel, British P. 313,269, 1928; *Brit. Chem. Abs. B*, 1929, 645.

<sup>39</sup> N. I. Voluinkin, Russian P. 26,029, 1932; *Chem. Abs.*, 1932, 26, 5730.

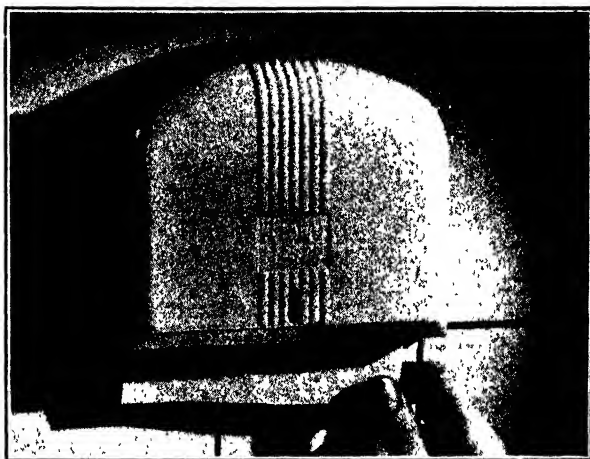
<sup>40</sup> L. E. Segond, French P. 765,534, 1934; *Chem. Abs.*, 1934, 28, 7044.

<sup>41</sup> H. Ford and R. H. McCarroll, British P. 365,828, 1931, to Ford Motor Co., Ltd.; *Brit. Chem. Abs. B*, 1932, 343.

<sup>42</sup> E. C. Rossiter, British P. 344,047, 1930, to Brit. Cyanides Co., Ltd.; *Brit. Chem. Abs. B*, 1931, 492.

similarly used by Hamoir<sup>43</sup> for making safety glass. Uncoated glass sheets can be united with an interposed film of plastic material containing on its surface a compatible synthetic resin adhesive, according to Moss and Crutchfield.<sup>44</sup>

A cold adhesive is formed from the condensation products of urea, thiourea, aldehydes, water and, if necessary, catalysts increasing the consistency of the adhesive.<sup>45</sup> Taylor and Keller<sup>46</sup> found that by heating urea, thiourea or their derivatives at 90°C. with paraformaldehyde in the presence of water or steam, a thin paste formed which could be evaporated to a syrupy consistency and then used as an adhesive or size. Layers of material can be bonded by the use of condensation products derived from polymerized formaldehyde and urea. A heat-treatment at 150°C. for 30 seconds effects the final hardening.<sup>47</sup> An adhesive containing nitrocellulose, a softening agent, a solvent and a urea-aldehyde condensation product



Courtesy Plaskon Co.

FIG. 108.—Towel Holder Made of a Urea-Formaldehyde Resin.

was prepared by Benteli.<sup>48</sup> Fuwa<sup>49</sup> employed a urea resin mixed with water glass and borax as an adhesive coating for the surface of ultraviolet-ray reflectors.

A network of organic fibers, such as wool or yarn, carrying a transparent or translucent synthetic resin prepared from urea and formaldehyde has been employed for cold frames used in horticulture.<sup>50</sup> An adhesive prepared from a urea resin and albumin can be used in making cellulose foils consisting of two layers of cellulose only one of which is capable of absorbing water.<sup>51</sup>

Browne and Hrubesky<sup>52</sup> found that by adding urea-formaldehyde condensation products to animal glues it was possible to render glued joints more water-re-

<sup>43</sup> R. P. P. V. Hamoir, French P. 696,787, 1929; *Chem. Abs.*, 1931, 25, 2827. See also French P. 673,668, 1928, to Soc. anon. des manuf. de Saint-Gobain, Chauny et Cirey; *Chem. Abs.*, 1930, 24, 2568.

<sup>44</sup> W. H. Moss and K. H. Crutchfield, U. S. P. 1,884,809, Oct. 25, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 1127.

<sup>45</sup> French P. 697,874, 1930, and 769,588, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3137; 1935, 29, 528.

<sup>46</sup> J. Taylor and A. V. Keller, British P. 331,428, 1929; *Brit. Chem. Abs. B*, 1930, 919. French P. 699,968, 1930; *Chem. Abs.*, 1931, 25, 3449.

<sup>47</sup> Allgem. Elektr.-Ges., British P. 316,194, 1928, to Int. Gen. Electric Co.; *Chem. Abs.*, 1930, 24, 1712.

<sup>48</sup> A. Benteli, Swiss P. 161,052, 1933; *Chem. Abs.*, 1934, 28, 592.

<sup>49</sup> K. Fuwa, Japanese P. 93,961, 1931, to Tokyo Denki K.K.; *Chem. Abs.*, 1933, 27, 1466.

<sup>50</sup> British P. 306,242, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 5019.

<sup>51</sup> R. Weingand, German P. 487,618, 1928, to Wolf & Co. Komm.-Ges.; *Chem. Abs.*, 1930, 24, 1979. See also German P. 578,873, 1933; *Chem. Abs.*, 1934, 28, 863.

<sup>52</sup> F. L. Browne and C. E. Hrubesky, *Ind. Eng. Chem.*, 1927, 19, 215.

sistant. A glue mixture containing urea-formaldehyde compositions gels like an untreated glue sol when it is chilled to room temperature while fluid. If the chilled jelly is kept at room temperature for a period longer than its working life, it cannot be melted again even on heating in a water-bath.

Baldwin<sup>66</sup> used a cement containing urea-formaldehyde resins in the production of linoleum and other floor coverings. A thin sheet material, e.g., paper, is placed on a supporting linoleum or felt base with an intervening cementing material containing a resin, a plasticizer and a modifier. Such a binder contains 50 parts of urea-formaldehyde resin, 25 parts of cumarone resin, 25 parts of rosin, 20 parts of tricresyl phosphate and 20 parts of dibutyl phthalate.

A resin developed by Eisenmann, Scholz and Wolf<sup>67</sup> for the production of abrasive paper is made by reacting hydroxyl-bearing esters of a fatty acid containing at least 10 carbon atoms with dimethylolurea in acid solution.

A method given by these investigators involves the preparation of an ester from one mol each of glycerol and linseed fatty acids. Then 250 parts of the ester are dissolved in 300 parts butyl alcohol and 50 parts ethyl alcohol; 13 parts of a 5 per cent solution (in ethyl alcohol) of urea nitrate are added, then 250 parts dimethylolurea. The batch is heated to 90°C. giving a solution of a resin. Later, 20 parts of tertiary sodium phosphate are added to neutralize. After settling, the phosphate is filtered off. A yellow-brown resin is obtained on evaporation of the solvent. Abrasive paper is made by applying to paper a 40 per cent toluol solution of the resin and distributing carborundum grains over the surface. The resinous adhesive is hardened by heating.

#### UREA RESINS USED WITH RUBBER

A composition of alkyd resins with urea-formaldehyde condensation products and emulsified rubber or rubber substitutes was found by Baird and Bunbury<sup>68</sup> to give flexible, semi-glossy coatings with good weathering qualities.

An alkyd-urea-formaldehyde resin is first made by heating 10 parts of alkyd resin, 20 parts of glycol monoethyl ether and 10 parts of dimethylolurea for about 30 minutes. The alkyd resin employed is prepared by heating 148 parts of phthalic anhydride, 62 parts of glycerol and 150 parts of castor oil at 190-200°C. for 3-4 hours while a current of carbon dioxide or nitrogen is passed through the reaction mixture. The coating is made by dissolving 30 parts of alkyd resin and 11 parts of the alkyd-urea-formaldehyde resin in 14 parts of solvent naphtha, 45 parts of butyl alcohol, 65 parts of water and 10 parts of rubber substitute emulsion and passing the stirred mixture through a colloid mill. The product can be applied by coating, dipping, spreading or spraying and is dried at temperatures above 90°C.

Uncured rubber cloth can be coated with a lacquer consisting of a polyhydric alcohol-polybasic acid resin, a hydroxylated fatty oil and a urea-formaldehyde condensation product.<sup>69</sup> The coating is hardened and the rubber is simultaneously vulcanized by treatment with a solution of sulphur chloride in carbon disulphide. Urea-aldehyde resins modified with phenols may be used, according to Thompson,<sup>70</sup> as adhesives for the attachment of rubber to metal, porcelain, glass or wood. The reaction product of thiourea and an aldehyde-ammonia serves, in small proportions, as an accelerator for the vulcanization of rubber.<sup>71</sup> Another group of accelerators

<sup>66</sup> J. T. Baldwin, U. S. P. 1,793,666 and 1,793,667, Feb. 24, 1931, to Sandura Co., Inc.; *Chem. Abs.*, 1931, 25, 2313.

<sup>67</sup> K. Eisenmann, E. Scholz and K. Wolf, U. S. P. 1,996,911, Apr. 9, 1935, to Unyte Corp. See also British P. 419,812, 1934, to Minnesota Mining & Mfg. Co.; *Chem. Abs.*, 1935, 29, 2682.

<sup>68</sup> W. Baird and H. M. Bunbury, British P. 349,903, 1929, to Imperial Chem. Ind.; *Brit. Chem. Abs. B*, 1931, 769.

<sup>69</sup> E. A. Bevan and W. J. S. Naughton, British P. 351,581, 1930, to Imp. Chem. Ind.; *Chem. Abs.*, 1933, 27, 447.

<sup>70</sup> O. A. Thompson, British P. 338,776, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 5909.

<sup>71</sup> N. A. Shepard and S. Krall, U. S. P. 1,647,784, Nov. 1, 1927, to Firestone Tire & Rubber Co.; *Chem. Abs.*, 1928, 22, 334.

is produced by mixing mercaptans or mercapto compounds with organic bases including thiourea and guanilyureas.<sup>66</sup>

By condensing urea with not more than 1 mol of formaldehyde in ammoniacal solution, Spiecker<sup>67</sup> obtained a preservative for latex. The material formed is soluble in water and remains liquid when concentrated as far as possible under reduced pressure. It is slowly decomposed on standing, evolving ammonia.

A resin formed from phenol glycerol ether, urea and formaldehyde increases the resistance of rubber masses to chemical and electrical influences.<sup>68</sup> By dispersing rubber in a liquid urea-formaldehyde resin, a plastic composition is obtained.<sup>61</sup>

### MISCELLANEOUS USES OF UREA RESINS

Rochet<sup>69</sup> reported the preparation of artificial silk directly from the condensation products of urea and formaldehyde.

As an example, 30 kg. of urea are dissolved in 80 l of commercial formalin, and the resulting solution is treated with calcium carbonate and filtered. The filtrate is refluxed for 3-4 hours in an apparatus fitted with a condenser. The condenser is then removed and the solution is further boiled until a test-sample gives a precipitate when poured into water. At this moment, 3 l. of a saturated solution of disodium hydrogen phosphate are added and the product is evaporated under reduced pressure until half of the water initially contained is removed. After cooling, the product is spun, using as a coagulating bath a saturated solution of magnesium sulphate (or sodium sulphate) to which sulphuric acid has been added until the solution turns bromophenol from blue to yellow. Cyanamide or dicyanodiamide can be used to replace the urea. Urea resins were incorporated by Dreyfus<sup>64</sup> in cellulose esters or ethers for the manufacture of silk films and threads.

The water-soluble types of urea resins are used in conjunction with deodorizing and preserving agents for the preservation of perishable animal products such as hides.<sup>64</sup> Taylor and Keller<sup>70</sup> employed a transparent, syrupy urea-aldehyde condensation product for the impregnation of leather. The treated material was dried, mixed with pigments and finally molded. Tanned leather was given an after-treatment with an aqueous solution of a urea-aldehyde condensate by Bergmann<sup>71</sup> in order to fix the residual tanning substances. Brunner and Scheele<sup>72</sup> applied urea-aldehyde resins to the preserving of physiological specimens (e.g., insects, plants, reptiles and fishes). The specimen is covered with a free-flowing resin and air is drawn from the interior of the specimen by evacuating. Finally, the liquid condensation product is converted into an insoluble solid by heating, and the transparent mass is polished. Urea and other fertilizers which are hygroscopic or have a tendency to cake during storage can be preserved by coating with a urea-formaldehyde condensate.<sup>68</sup>

<sup>66</sup> British P. 284,740, 1926, to Rubber Service Labs. Co.; *Chem. Abs.*, 1929, 23, 732.

<sup>67</sup> F. W. Spiecker, German P. 570,473, 1928; *Chem. Abs.*, 1933, 27, 3541.

<sup>68</sup> Swiss P. 165,712, 1934, addn. to 163,553, to J. R. Geigy A.-G.; *Chem. Abs.*, 1934, 28, 2946.

<sup>64</sup> D. F. Twiss and J. A. Wilson, British P. 403,142, 1933, to Dunlop Rubber Co., Ltd.; *Chem. Abs.* 1934, 28, 3197.

<sup>69</sup> J. Rochet, U. S. P. 1,951,994, Mar. 20, 1934, to Comp. de prod. chim. & électromét. Alais, Frogeat & Camargue; *Chem. Abs.*, 1934, 28, 3586. German P. 536,754, 1929; *Chem. Abs.*, 1932, 26, 1121. French P. 712,005, 1930; *Chem. Abs.*, 1932, 26, 2054. British P. 305,468, 1929; *Brit. Chem. Abs. B*, 1930, 813.

<sup>70</sup> H. Dreyfus, French P. 39,023, addn. to 702,174; *Chem. Abs.*, 1932, 26, 1784.

<sup>71</sup> German P. 534,889, 1926, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 1046. Swiss P. 127,967, 1926, addn. to 124,636; *Chem. Abs.*, 1929, 23, 2257.

<sup>72</sup> J. Taylor and A. V. Keller, British P. 333,759, 1929; *Brit. Chem. Abs. B*, 1930, 1081.

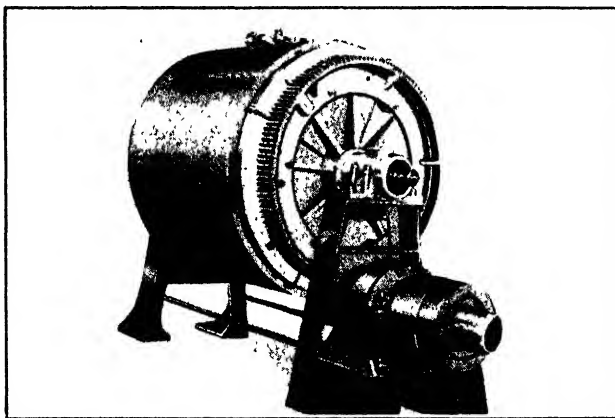
A. M. Bergmann, U. S. P. 1,947,513, Feb. 20, 1934; *Chem. Abs.*, 1934, 28, 2568. M. Bergmann and A. Miekeley, German P. 606,140, 1934; *Chem. Abs.*, 1935, 29, 1078.

<sup>73</sup> J. Brunner and E. Scheele, U. S. P. 1,583,164, June 8, 1926; *Chem. Abs.*, 1926, 20, 2515. British P. 263,674, 1926; *Brit. Chem. Abs. B*, 1927, 208.

<sup>74</sup> British P. 339,163, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 40.

Prüfer and Dulik<sup>66</sup> extended the use of urea resins to the production of light-sensitive layers for photographic purposes. Thus, 20 cc. of a solution of a urea-aldehyde condensation product that is soluble in warm water and contains the equivalent of 20-30 per cent of solid urea are heated and emulsified with silver halide. The product is cooled, washed and finally applied while warm to glass, film or paper. If a copy is to be made on a plate of zinc or copper, the metal is first thoroughly cleaned and then is covered with a chromated resin solution which is composed of 10 cc. of a urea resin containing 12-15 per cent of solid urea and diluted with 5-10 cc. of water, 2 cc. of a 10-20 per cent solution of ammonium dichromate, 2 drops of a 5 per cent albumin solution and 2 drops of a 10 per cent solution of copper bromide (acting as an accelerator). The plate is next dried in a centrifuge. A copy is made from a ruled negative in daylight or with artificial light and is developed for a few seconds under a water-jet. After the copy has been colored with an aqueous solution of a dyestuff and subsequently dried, the etching can be effected without a previous treatment with heat.

Ink for use in intaglio printing can be prepared by incorporating finely divided or dissolved coloring matter with a urea resin dissolved in a volatile, organic



Courtesy Paul O. Abbé, Inc.

FIG. 109.—Large-size Pebble Mill, Jacketed for Temperature Control, and with Inching-Type Motor Drive for Grinding Urea Plastics.

solvent.<sup>70</sup> The solvents employed are alcohols (with less than 6 carbon atoms in the molecule), ketones and esters or hydrocarbons of the aromatic series. Thus, lampblack and the calcium salt of an azo dyestuff prepared from aniline and 2,6-naphtholsulphonic acid are triturated with a urea-formaldehyde condensation product dissolved in a mixture of isobutanol and ethanol. Laking of dyes with urea resins has been mentioned previously. Water-soluble urea-formaldehyde resins were used by Reindel and Ohmer<sup>71</sup> in the preparation of color lakes from acid dyes.

Films may be manufactured from urea-aldehyde resins by applying viscous solutions of the latter, preheated to 100°C., to a travelling base and allowing them to solidify.<sup>72</sup> This solidification is effected at temperatures of 70-100°C.,

<sup>66</sup> H. Prüfer and K. Dulik, U. S. P. 1,964,136, June 26, 1934; *Chem. Abs.*, 1934, 28, 4993. See also I. Kreidl, C. Rosen and K. Rutter, British P. 403,664, 1933, to Verein. chem. Fabr. Kreidl, Heller & Co.; *Chem. Abs.*, 1934, 28, 3606. French P. 739,004, 1932; *Chem. Abs.*, 1933, 27, 1837.

<sup>70</sup> H. Fleischmann and O. Jordan, U. S. P. 1,787,239, Dec. 30, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 833. British P. 307,877, 1929; *Brit. Chem. Abs. B*, 1930, 26. French P. 671,082, 1929; *Chem. Abs.*, 1930, 24, 1996. Cf. the use of urea-formaldehyde resins in transfer inks. French P. 774,431, 1934, to British Cyanides Co., Ltd., and H. E. Peace & Co., Ltd.; *Chem. Abs.*, 1935, 29, 2266.

<sup>71</sup> H. Reindel and A. Ohmer, U. S. P. 1,974,510, Sept. 25, 1934, to General Aniline Works; *Chem. Abs.*, 1934, 28, 7554.

<sup>72</sup> R. Weingand, British P. 318,580, 1928, to Wolff & Co.; *Chem. Abs.*, 1930, 24, 2256. British P. 298,631, 1927; *Chem. Abs.*, 1929, 23, 2990. French P. 661,598, 1928; *Chem. Abs.*, 1930, 24, 476.



the films being removed when no longer sticky on the surface. Softening agents (glycerol or methylcyclohexyl adipate) should be added to the resin.

Various other applications of urea resins have been suggested. Goldscheider and Tuschinsky<sup>73</sup> prepared imitation frosted or stained glass by impregnating wire gauze or a fabric with a urea-formaldehyde-resin lacquer and applying granulated glass to the surface. Fibrous materials, soaked with urea- or thiourea-formaldehyde condensation products and then hot-molded with small quantities of an acid condensing agent, were proposed as brake linings.<sup>74</sup> As referred to in the section on the impregnation of paper, acoustic diaphragms for use in telephone transmitters can be manufactured from urea condensation products.<sup>75</sup> Rickets<sup>76</sup> prepared such diaphragms by treating paper, linen, silk, artificial silk or mercerized cotton with a urea or thiourea resin. Artificial cork masses can be manufactured by impregnating cork meal with less than 30 per cent of its weight of unhardened urea resin together with a softening or plasticizing agent (e.g., glycerol) and compressing the resultant composition.<sup>77</sup> Aqueous solutions of urea resins mixed with acids and acid salts are employed in the treatment of wood.<sup>78</sup> A layer of urea resin with added pigments has been used as a coating for ebonite panels to prevent deterioration by light.<sup>79</sup>

A product obtained by condensing urea with hexamethylenetetramine was used by Mossgraber<sup>80</sup> as a protective colloid for dispersions of metals or metalloids in organic liquids such as glycol, glycerol, hydrocarbons and animal or vegetable oils. The oily substance obtained by the prolonged refluxing of formaldehyde solution with di-o-tolylthiourea was employed by Schmidt<sup>81</sup> as an inhibitor for sulphuric acid pickling baths. Schlacht<sup>82</sup> applied coatings of urea resins as a preservative for soil profiles. A sheet of celluloid is coated with a solution of the colorless, water-soluble urea resin and is pressed against a vertical, smoothly-faced profile wall. After 5-10 minutes, the sheet is peeled off with a thin layer of soil adhering. When this sheet is dried, a permanent "monolith" of the profile is obtained.

<sup>73</sup> R. Goldscheider and I. Tuschinsky, British P. 246,012, 1926; *Chem. Abs.*, 1929, 23, 254.

<sup>74</sup> French P. 696,705, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2825.

<sup>75</sup> W. E. Goodwin, British P. 329,429, to Siemens Bros. & Co.; *Chem. Abs.*, 1930, 24, 5445.

<sup>76</sup> W. J. Rickets, British P. 302,746, 1927; *Chem. Abs.*, 1929, 23, 4309.

<sup>77</sup> British P. 322,752, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1930, 138.

<sup>78</sup> K. Vierling, M. Schmiling and H. Klungenberg, German P. 550,647, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4932.

<sup>79</sup> P. E. Wells, British P. 303,814, 1927, to Brit. Hard Rubber Co., Ltd.; *Chem. Abs.*, 1929, 23, 4542.

<sup>80</sup> E. Mossgraber, German P. 581,416, 1933, to Allgem. Elekt.-Ges.; *Chem. Abs.*, 1933, 27, 5125.

<sup>81</sup> J. G. Schmidt, U. S. P. 1,807,711, June 2, 1931, to E. F. Houghton & Co.; *Chem. Abs.*, 1931, 25, 4216.

<sup>82</sup> K. Schlacht, *Z. Pflanz. Dunc.*, 1929, 13A, 426; *Brit. Chem. Abs. B.*, 1929, 756.

## Chapter 31

### Thiourea Resins. Mixed Urea-Thiourea Resins

Thiourea, because of the water-resistance that it imparted, was heralded as an all-important constituent of molding compositions,<sup>1</sup> but it has proved somewhat intractable from the standpoint of the molder. Ordinary molds (see Chapter 28) are stained by thiourea-containing powders, necessitating the use of stainless steel or chromium plated molds. Thus, the molder was unable to employ his usual equipment and faced the necessity of purchasing new and more expensive molds. Another feature handicapping the development of thiourea-formaldehyde moldings is their characteristic slow rate of cure. Thiourea resins require a curing time of about ten minutes, comparing very unfavorably with the rapidity with which Bakelite resins cure. As the molding industry has developed largely along the lines of piece work, the time involved in individual operations seriously affects the cost of the final product and the profit derived therefrom. Since urea resins cure much faster than thiourea products, the expedient of preparing a resin containing both urea and thiourea was tried. The composite resin cured more expeditiously and was resistant to water, but still exerted a deleterious action on the mold. In modern practice, water-resistant ware can be fabricated from urea resins alone, and hence thiourea-formaldehyde condensates are no longer manufactured extensively.

#### PRODUCTION OF THIOUREA AND RELATED COMPOUNDS

Thiourea, as synthesized by Claus<sup>2</sup> in 1873, was a colorless crystalline compound melting at 172°C. It dissolved in water, was slightly soluble in alcohol and difficultly soluble in ether. Inghilleri<sup>3</sup> described the synthesis of thiourea and ammonium thiocyanate by heating carbon disulphide and ammonium carbonate. Ammonium dithiocarbamate is first formed and is converted successively into ammonium thiocyanate and thiourea by further heating.

The conversion of ammonium thiocyanate to thiourea (analogous to Wöhler's synthesis of urea) is conducted extensively on a commercial scale, since the wet process for the purification of illuminating gas offers a readily available supply of the thiocyanate.<sup>4</sup> A 35 per cent solution of ammonium thiocyanate obtained as a by-product in the gas industry is crystallized by concentration in a resistant vessel made of a non-ferrous metal. The crystals are then heated for several hours at 140-160°C. under atmospheric or reduced pressure. A 25 per cent yield of thiourea is obtained and separated from the unchanged thiocyanate which is further treated with heat. Donauer prepared thiourea by heating ammonium

<sup>1</sup> See a review by K. M. Chance, *Australian Plastics and Allied Trades Rev.*, 1933, 2 (2), 13; *Chem. Abs.*, 1934, 28, 533. Although resins made from urea and thiourea represent a type of amino linkage forming aminoplasts of a similar character generically considered (see Chapter 28), it should be noted that despite their general equivalency thiourea possesses certain disadvantages which render it less useful than urea for various molding purposes.

<sup>2</sup> Claus, *Ber.*, 1873, 6, 727. The melting point of thiourea is now considered to be 182°C. See, for example, "International Critical Tables," McGraw-Hill Book Co., N. Y., 1928, I, 177.

<sup>3</sup> G. Inghilleri, *Gazz. chim. ital.*, 1909, 39 (1), 634; *Chem. Abs.*, 1911, 5, 696.

<sup>4</sup> *British Plastics*, 1934, 5, 550.

thiocyanate *in vacuo* at 160°C., then allowing the material to cool slowly to 110-120°C. when it was granulated.<sup>4</sup> The cooled product was added to sufficient water at 10-14°C. to maintain the unchanged ammonium thiocyanate in solution at -10°C. The undissolved material was then crystallized from hot water, yielding thiourea. A large proportion of the thiourea industrially produced is prepared from crude calcium cyanamide (see Fig. 110). If this compound is dissolved in water at a temperature low enough to prevent the substantial decomposition of the cyanamide

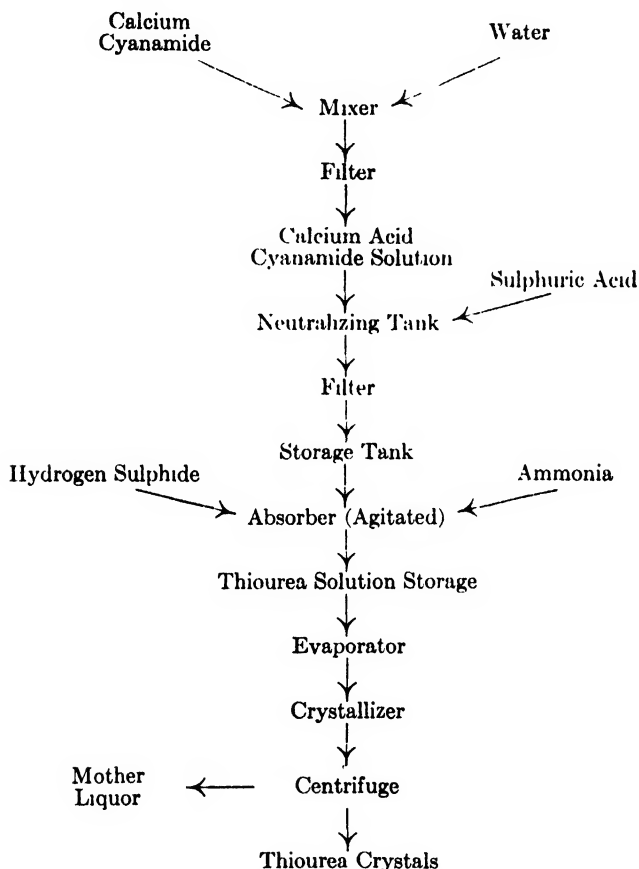


FIG. 110.—Flow Diagram for the Preparation of Thiourea from Calcium Cyanamide.  
(R. V. Heuser.)

present, filtered and treated with a solution containing sulphur and ammonium sulphide, thiourea is formed.<sup>4a</sup> A process described by Heuser<sup>5</sup> utilized hydrogen sulphide and ammonia in conjunction with the cyanamide solution to form thiourea. Mayen and Wolfes<sup>6</sup> prepared an aqueous cyanamide solution, first, by extracting

<sup>4</sup> M. Donauer, U. S. P. 1,949,738, March 6, 1934, to Koppers Co.; *Brit. Chem. Abs.* B, 1935, 92.

<sup>4a</sup> F. S. Washburn, U. S. P. 1,607,326, Nov. 16, 1926; *Chem. Abs.*, 1927, 21, 249.

<sup>5</sup> R. V. Heuser, U. S. P. 1,991,852, Feb. 19, 1935, to American Cyanamid Co.; *Chem. Abs.*, 1935, 29, 2180. See also G. A. Kirkhof and E. A. Akonantz, *Khm. Farm. Prom.*, 1934 (3), 17; *Chem. Abs.*, 1935, 29, 1781.

<sup>6</sup> H. Mayen and O. Wolfes, German P. 452,025, 1924, to E. Merck; *Brit. Chem. Abs.* B, 1930, 315. See also W. Schulenburg, U. S. P. 1,977,210, Oct. 16, 1934; *Chem. Abs.*, 1935, 29, 181.

calcium cyanamide at 15°C. and precipitating the calcium with carbon dioxide. The filtered solution is then saturated (at 15-60°C.) with hydrogen sulphide in the presence of water-soluble bases (ammonia). After concentration, the thiourea is deposited in the form of crystals. In another preparative method,<sup>7</sup> calcium sulphide is added to an aqueous solution of calcium cyanamide, and carbon dioxide is led in at a pressure of 5 atmospheres and a temperature of 75°C. The nascent hydrogen sulphide produced reacts with the cyanamide to form thiourea. A similar procedure<sup>8</sup> entails adding calcium cyanamide and calcium sulphide (in the theoretical proportions) to 5 times their weight of water, treating with carbon dioxide to precipitate all the calcium and then heating at 75°C. for 1-1.5 hours with stirring. The thiourea is recovered by filtration and evaporation.

Flemming and Klein<sup>9</sup> described the preparation of thioureas from mustard oils and diarylguanidines, in inert solvents at temperatures below the decomposition points of the products. The method is more applicable to complex, substituted types. Thus, N,N'-di-o-tolyl-N''-phenylthiocarbamidoguanidine (m. p. 179-180°C.) was obtained in 93 per cent yield from di-o-tolyl-guanidine and phenyl mustard oil in boiling benzene. Diarylthioureas are formed by treating carbon disulphide with an excess of an amine, without using neutral solvents or water.<sup>10</sup> Aniline, e.g., gives thiocarbanilide with carbon disulphide.

The vapor-phase reactions of carbon disulphide and aniline were employed by O'Brien<sup>11</sup> in the production of thioureas. Carbon disulphide vapor is introduced at the bottom and aniline at the top of a tower divided into a number of compartments, connected by pipes arranged to insure an intimate mixing of the reactants. The temperature of the tower is maintained at about 130°C. by electric heating coils or superheated steam. Hydrogen sulphide escapes through the top of the tower, and the reaction product (diphenylthiourea) flows down into a trap containing benzene, from which it is separated and dried. A catalytic carbon disulphide-amine process for thiourea was developed by Hand and Roberts.<sup>12</sup> Aromatic amines are heated at 46°C. with 60 per cent of carbon disulphide in the presence of an alkaline catalyst volatile below 75°C. (0.1-0.25 per cent of concentrated ammonia solution). The evolved hydrogen sulphide vapors are scrubbed by passing through a tank containing a second charge of amine and catalyst, this charge being admitted to the mixer when the reaction is complete in the first charge and the excess of carbon disulphide and catalyst have been recovered by distillation at 75°C. Bedford and Sibley<sup>13</sup> employed a p-nitroso compound (p-nitrosophenol or p-nitrosodimethylaniline) to remove the hydrogen sulphide formed in the condensation of aniline and carbon disulphide. The hydrogen sulphide combines with the nitroso compound, aniline and carbon disulphide to form a derivative of thiocarbanilide. This removal of hydrogen sulphide accelerates the production of thiocarbanilide. The mechanism of the carbon disulphide-aniline reaction was studied by Snedker<sup>14</sup> who postulated the following reactions:

<sup>7</sup> French P. 630,883, 1927, to Soc. d'Etudes Chim. pour l'ind.; *Brit. Chem. Abs. B*, 1930, 409.

<sup>8</sup> Swiss P. 119,471, 1926, to Comp. de l'Azote et des Fert. Soc. anon.; *Brit. Chem. Abs. B*, 1929, 200.

<sup>9</sup> W. Flemming and H. Klein, German P. 464,319, 1928, to Silesia Verein chem. Fabr.; *Chem. Abs.*, 1928, 22, 4133.

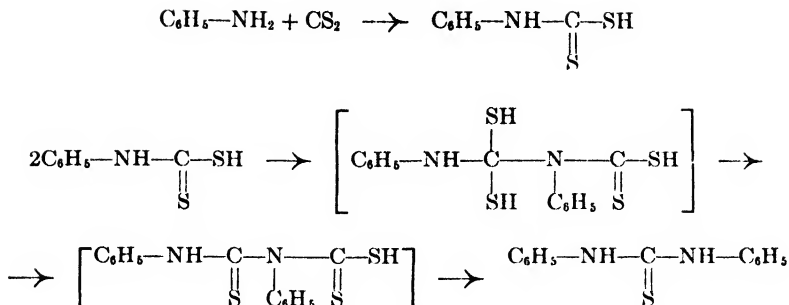
<sup>10</sup> British P. 207,906, 1928, to Silesia Verein chem. Fabr.; *Chem. Abs.*, 1930, 24, 131. Carboditolylimide was used by G. H. Stevens (U. S. P. 1,856,596, May 3, 1932; *Chem. Abs.*, 1932, 26, 3699) as an accelerator in the vulcanization of rubber.

<sup>11</sup> W. G. O'Brien, U. S. P. 1,482,317, Jan. 29, 1924, to Goodyear Tire & Rubber Co.; *J.S.C.I.*, 1924, 43, 353B.

<sup>12</sup> C. N. Hand and H. P. Roberts, U. S. P. 1,688,707, Oct. 23, 1928, to Rubber Service Labs. Co.; *Brit. Chem. Abs. B*, 1929, 511. C. N. Hand and C. E. Smith, U. S. P. 1,724,580, Aug. 13, 1929; *Chem. Abs.*, 1929, 23, 4710.

<sup>13</sup> C. W. Bedford and R. L. Sibley, U. S. P. 1,477,804, Dec. 18, 1923, to Goodyear Tire & Rubber Co.; *J.S.C.I.*, 1924, 43, 233B.

<sup>14</sup> B. J. C. Snedker, *J.S.C.I.*, 1925, 44, 74T.



Uedinov, Drozdov and Stepanov,<sup>15</sup> in a study of the same reaction, found that a maximum yield of thiocarbaniide was obtained with a 10-20 per cent excess of carbon disulphide, but an excess of aniline greatly reduced the yield owing to a tendency to form triphenylguanidine. Diphenylguanidine is made by treating aniline with cyanogen chloride, distilling the excess aniline and adding a weak alkali.<sup>16</sup> The reaction of a mercaptan and a cyanamide in aqueous or alcoholic solution yields isothiourea ethers.<sup>17</sup> The mercaptan is passed in vapor form through the solution. S-Ethyl-isothiourea is thus obtained from ethylmercaptan and cyanamide. In a spectroscopic study of thiourea, Rivier and Borel<sup>18</sup> concluded that thiourea and trimethylthiourea can exist only in the *iso* state and do contain the C=S group. Thiourea derivatives<sup>19</sup> may be prepared by heating the mineral acid salts of amines such as aniline hydrochloride, p-phenetidine hydrochloride and 4-amino-indazole hydrochloride with an alkali thiocyanate in the presence of an inert organic solvent.

### THIOUREA RESINS

The conditions under which urea or thiourea will form resins with formaldehyde which can be used in molding are limited and must be carefully controlled. According to Novotny and Wilson,<sup>20</sup> the condensation markedly tends to form a gel, from which the mother liquor may be removed only with difficulty. Catalysts increase this tendency, and even when the water is removed, the resin is liable to be almost infusible and of little use for molding. As a result, many of these products, as described later, are cast rather than molded.

Novotny and Wilson developed a method of removing water from the liquid condensate without promoting gel formation. The reaction between thiourea and formaldehyde is carried out in a slightly alkaline medium without heating. Specifically, 1 part of barium hydroxide is dissolved in 160 parts of 36 per cent formalin and 120 parts of thiourea are added with stirring. The temperature of the mixture is held below 40°C. and the reaction is complete in 2 hours. To counteract the slight acidity that may develop, 2 parts of ammonium hydroxide (sp. gr. 0.9) are added, giving a stable solution that may be kept for long periods. Carbon dioxide is led into the mixture to precipitate barium carbonate. The clear solution, prior to its evaporation, serves as a varnish and an impregnant (e.g., in the preparation of laminated materials). Water may be removed from the aqueous condensate by freezing or by evaporation, giving an almost colorless, brittle product. The freezing treatment

<sup>15</sup> M. N. Uedinov, N. S. Drozdov and N. A. Stepanov, *J. Chem. Ind. (Moscow)*, 1929, 6, 37; *Chem. Abs.*, 1929, 23, 3214.

<sup>16</sup> R. V. Heuser, U. S. P. 1,727,060, Sept. 3, 1929, to American Cyanamid Co; *Brit. Chem. Abs. B*, 1929, 916.

<sup>17</sup> British P. 296,782, 1927, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1929, 23, 2447.

<sup>18</sup> H. Rivier and J. Borel, *Helv. Chim. Acta*, 1928, 11, 1219; *Chem. Abs.*, 1929, 23, 1115.

<sup>19</sup> British P. 414,462, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 481.

<sup>20</sup> E. E. Novotny and W. C. Wilson, U. S. P. 1,926,786, Sept. 12, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 5996.

yields a mixture of ice and resin which is then finely divided in an impact pulverizer and carried through currents of air (air flotation) until the ice melts, separating from the resin particles. The resin is recovered in a cyclone separator as a fine powder. One advantage of this method is the possibility of control of the condensation which may be stopped at any point by subjection to the freezing process. The non-gelling character of the solution permits recovery of the resin by spraying the liquid through nozzles into a heated room or into a heated cyclone separator.

A relatively early description of the use of thiourea in conjunction with formaldehyde for resin formation is contained in the work of John,<sup>21</sup> who heated 1 part of urea or thiourea with 5 parts of commercial formalin until a part of the water had distilled and a glue-like mass remained. Prolonged heating gave a glassy, insoluble material.

A solution of a thiourea-formaldehyde resin capable of heat-hardening and applicable as a varnish was produced by Schmidt<sup>22</sup> by carrying out the condensation in an appropriate solvent. Thus, 100 parts of thiourea (part of which may be replaced by urea) are dissolved in 100 parts of ethyl lactate and a like amount of the mono-ethyl ether of ethylene glycol. Then 60 parts, by weight, of paraform are added, and the mixture is refluxed for 2-3 hours and filtered. The resulting solution can be used directly as a varnish, as a lacquer (with thinners) or as a component of molding mixtures.

The condensation is not necessarily carried out in a solvent. An aqueous solution of formaldehyde (e.g., 650 g. of a 40 per cent solution) may be refluxed with thiourea (300 g.) for 1.5 hours.<sup>23</sup> The addition of 1000-1500 cc. of water precipitates the resin, which is fusible at 100°C. and soluble in the organic resin solvents. This non-reactive resin is dissolved in a solvent, capable of dissolving paraformaldehyde, for further treatment. Paraform (50-75 parts) is added to the solution which is then useful as a varnish or impregnant. The films prepared by hardening this resin are resistant to alcohol, acetone and benzene. The almost universal presence of formic acid in commercial formaldehyde which often gives the thiourea-formaldehyde resins an undesirable acid reaction caused Rossiter<sup>24</sup> to attempt to remove it without the use of alkali by passing a stream of dry air or an inert gas through the liquid condensate during evaporation below 100°C. As with resins from urea itself, if thiourea and aqueous formaldehyde are condensed, the first product is water-soluble and may be concentrated to a syrup.<sup>25</sup> This syrup is converted into a moldable material by adding a filler and an acid substance. The dried product, containing the condensate, wood flour and oxalic acid, sodium hydrogen sulphate, potassium tetroxalate or aniline hydrochloride as hardening substances, is hot-molded.

A mixture of thiourea and urea may be employed to replace thiourea, or the two substances can be condensed separately with formaldehyde, and the water-soluble, initial condensates mixed in solution.<sup>26</sup> The mixture is concentrated by evaporation. As noted earlier in the chapter, slow curing is a disadvantage of thiourea resins; however, the combined urea-thiourea-formaldehyde resin cures more rapidly and yet retains the solubility of the purely thiourea-formaldehyde combinations. If 25 per cent or less of the thiourea is replaced by urea, clear

<sup>21</sup> H. John, U. S. P. 1,355,834, Oct. 19, 1920; *Chem. Abs.*, 1921, 15, 418.

<sup>22</sup> J. H. Schmidt, U. S. P. 1,818,360, Aug. 11, 1931, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 5585. German P. 569,835, 1930; *Chem. Abs.*, 1933, 27, 858. J. H. Schmidt and R. S. Daniels, Canadian P. 313,958, 1931; *Chem. Abs.*, 1931, 25, 5305. Canadian P. 322,449, 1932; *Chem. Abs.*, 1932, 26, 3636. British P. 368,898, 1930; *Brit. Chem. Abs. B*, 1932, 118.

<sup>23</sup> J. H. Schmidt and R. S. Daniels, U. S. P. 1,944,867, Jan. 23, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 2205.

<sup>24</sup> E. C. Rossiter, British P. 243,477, 1924, to Brit. Cyanides Co., Ltd.; *Chem. Abs.*, 1927, 21, 828.

<sup>25</sup> E. C. Rossiter, British P. 258,950, 1928, to Brit. Cyanides Co.; *Chem. Abs.*, 1927, 21, 8276.

<sup>26</sup> E. C. Rossiter, British P. 266,088, 1926, to Brit. Cyanides Co.; *Chem. Abs.*, 1928, 22, 506. German P. 559,362, 1932; *Chem. Abs.*, 1934, 28, 270. Canadian P. 274,738, 1927; *Chem. Abs.*, 1927, 21, 4079.

resin syrups are formed, but above this figure turbid products, which still cure rapidly, result. The turbidity is obviated by the incorporation of a small amount of ammonia. Traces of acid or alkali do not affect the solubility of thiourea resins. In an example illustrating the preparation of mixed resins, 95 lb. of thiourea and 74 lb. of urea are dissolved in 371 lb. of formalin containing 120 lb. of formaldehyde. The mixture is warmed to 50-70°C. until all the thiourea and urea have

FIG. 111.—  
Hydraulic Press Used in Making  
Laminated Sheets.



*Courtesy Bakelite Corp.*

dissolved. The turbid solution obtained after standing a few hours to effect condensation is evaporated at 70-80°C. by blowing a brisk current of air through it until the required consistency is reached.

From 2 to 10 per cent of free thiourea has been added to function as an accelerator in urea-aldehyde reaction products which are being ground in preparation for molding.<sup>27</sup>

Gams and Widmer<sup>28</sup> also described a method of resin formation based on the use of urea and thiourea. The formaldehyde is first condensed with not more than 1 mol of urea (per mol of aqueous formaldehyde) at a temperature of 100°C. until a sample

<sup>27</sup> E. C. Rossiter, British P. 351,094, 1930, to Brit. Cyanides Co.; *Chem. Abs.*, 1932, 26, 5392.

<sup>28</sup> A. Gams and G. Widmer, U. S. P. 1,854,896, Apr. 19, 1932, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 2392. British P. 275,995, 1927; *Brit. Chem. Abs. B*, 1927, 219.

of the reaction mixture yields a precipitate on dilution with water. Thiourea is then added to bring the total amount of urea and thiourea to 1 mol for each 1.6 mols of formaldehyde, and the solution is evaporated and hardened. These proportions enable clear, glassy resins to be prepared from a minimum amount of formaldehyde. With urea and formaldehyde alone, a departure from the ratio of 2 mols of formaldehyde per mol of urea gives non-glassy or even milky films. Restriction of the amount of formaldehyde by using a urea-thiourea combination frees the final products from objectionable aldehyde odors. A small amount (less than 1 per cent) of ammonium sulphate or ammonium thiocyanate added with the thiourea serves as a catalyst in hardening the resin. At the time of adding the thiourea, a considerable amount of free aldehyde is present in the solution. The fixation of the formaldehyde is normally accelerated by heating, but if the solution is made neutral or feebly alkaline, a slow reduction of the quantity present ensues on standing.<sup>20</sup> By this treatment, the resins give water-resistant varnishes. Thus, 120 parts of urea are dissolved in 334 parts of 36 per cent formaldehyde, mixed with 30 parts of blood charcoal and filtered. The clear solution is heated for 6 hours at 98°C. in an autoclave equipped with a stirring device. After neutralizing the product to litmus with a dilute sodium hydroxide solution, 45 parts of thiourea are added. On standing for 2 days at room temperature, the free formaldehyde is reduced from 6 per cent to 0.5 per cent by volume, and the viscosity of the solution remains unchanged.

Kraus<sup>20</sup> described the preparation of resins, that can be molded under heat and pressure, by boiling urea, thiourea and urethan with aqueous formaldehyde in the presence of an acid catalyst (acetic acid) until a hydrophobe product separated on cooling. The products of the reaction are rapid-hardening, water-stable resins.

An additional method<sup>21</sup> of preparing urea-thiourea resins includes the use of a mixture of 1 mol of urea and 1 mol of thiourea pretreated in non-acid solution with 2 mols of formaldehyde. This is then gradually added to a hot solution of 1 mol of urea and less than 2 mols of formaldehyde containing an acid condensing agent. The final molar ratio should be 1 mol of total urea and thiourea to 1.4-1.8 mols of formaldehyde. Specifically, 300 parts of urea are dissolved in 1500 parts of previously neutralized, 30 per cent formaldehyde, and 5 parts of 10 per cent acetic acid are added. After heating to the boiling point, a solution of 562 parts of thiourea and 450 parts of urea in 1500 parts of neutral formalin is introduced during a period of 15-30 minutes, and the boiling is continued for 45-60 minutes. At the end of this time, there are formed hydrophobe masses which precipitate on cooling. The precipitated condensate is mixed with cellulose, dried at a low temperature, ground and hot-molded.

A two-stage reaction of thiourea and urea with formaldehyde was carried out by Smidth.<sup>22</sup> First, 225 grams of urea are dissolved at a temperature of 25-50°C. in 640 cc. of a slightly acid, 35 per cent formaldehyde solution. This mixture is then vacuum distilled below 100°C. to remove most of the water. Next, 63 g. of thiourea are added and a second vacuum distillation is performed at 150°C. until nearly all of the water is removed and the product is as viscous as possible (but still can be cast). The resin, cast under pressure, is hard and brittle, but comparatively soluble. It is finally heat-treated at 95°C. for three days and is transformed into a transparent, tough, insoluble and infusible product. Before final hardening, the cast resin may be ground, mixed with fillers and modifiers and molded.

A variation of this method, designed to improve the water-resistance of the

<sup>20</sup> A. Gams, G. Widmer and K. Frey, U. S. P. 1,890,033, Dec. 6, 1932, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1933, 27, 1724. British P. 313,615, 1929; *Brit. Chem. Abs. B*, 1930, 1120. Swiss P. 140,428, 1928; *Chem. Abs.*, 1931, 25, 1045. French P. 638,082, 1927; *Chem. Abs.*, 1929, 23, 248. French P. 37,012, 1929, addn. to 638,082; *Chem. Abs.*, 1931, 25, 1047.

<sup>21</sup> W. Kraus, British P. 383,025, 1932; *Chem. Abs.*, 1933, 27, 4431.

<sup>22</sup> Kunsthfabr. F. Pollak G.m.b.H., British P. 375,609, 1932, to Pollopos Ltd.; *Chem. Abs.*, 1933, 27, 3837. French P. 719,139, 1931; *Chem. Abs.*, 1932, 26, 3392.

<sup>23</sup> L. Smidth, U. S. P. 1,704,847, Mar. 5, 1929, to E. G. Budd Mfg. Co.; *Chem. Abs.*, 1929, 23, 2000. Reissue 18,943, Sept. 12, 1933; *Chem. Abs.*, 1933, 27, 5907. British P. 294,253, 1928; *Brit. Chem. Abs. B*, 1929, 1047. French P. 657,818 and 657,844, 1923; *Chem. Abs.*, 1929, 23, 4542.



resins, entails the condensation of 2 mols of slightly acid, aqueous formaldehyde with 1 mol of urea and, after a few minutes, the addition of 0.2 mol of thiourea.<sup>33</sup> When almost all of the water has been removed by vacuum distillation, formic acid is added, and the mixture is cast in molds and subsequently dried in an oven. Kelley and Deisley<sup>34</sup> developed a further modification of the preparation of urea-thiourea-formaldehyde condensation products. A mixture with a  $p_H$  of 5.2-7.0, containing urea, formaldehyde and ammonia solution, is first heated under reflux for a short time. Thiourea is then added, and refluxing is continued until a test sample no longer dissolves in water. The next step is the addition of a salt of a strong base and a weak acid (sodium acetate) in order to retard the gelation of the homogeneous, liquid condensate. By vacuum evaporation, 20 per cent of the water is removed, and the excess formaldehyde is converted by adding urea. As soon as 30 per cent of the aldehyde has reacted with urea, formic acid is introduced, and the concentration of the material is continued until the substance can be cast while hot in a mold. Other acids or acid salts (e.g., potassium phosphate or aluminum chloride) may replace formic acid in the final phase of the process. A molding composition suggested by Belfit<sup>35</sup> is prepared as follows. Urea and formaldehyde are condensed in solution at a  $p_H$  of 5.5 or higher at 110-120°C. under pressure. Then a minor percentage of thiourea is added to the solution, followed by a fibrous filler and a dye. The mixture is duly dried below 100°C and ground to 20- or 30-mesh.

Water-resisting resins were also produced by Rothera, Blythen and Gillespie<sup>36</sup> through heating a mixture of urea and thiourea (previously treated with alkaline formaldehyde solution) with acids. The heating is continued until the resin precipitates on cooling, and the products are further processed and hardened. Mains<sup>37</sup> used a 30-60 per cent solution of a urea-thiourea resin to impregnate wood for making trays and boxes. Fireproof paneling<sup>37</sup> may be made by impregnating asbestos and wood veneer with a heat hardenable urea-thiourea resin and pressing the sheets together. A method not necessitating the admixture of urea consists in the condensation of 1 mol of thiourea with 1.5 mols of aqueous formaldehyde at a  $p_H$  of 3.<sup>38</sup> The solution, to which volatile solvents are added, is used for the impregnation of fabrics and asbestos. The material obtained is dried at a low temperature and consolidated by hot-pressing, or is disintegrated to form molding and die-casting powders. Thiourea is added, in another method, in the final concentration of the syrup formed from 2 mols of formaldehyde and 1 of urea.<sup>39</sup> Sisley<sup>40</sup> prepared a mordant by condensing thiourea and an aliphatic aldehyde (formaldehyde, acetaldehyde or crotonaldehyde) in the presence of a mineral acid. The product may be used on wool, silk, leather or furs but not on cellulose acetate.

Eisenmann and Kuchenbuch<sup>41</sup> have also prepared thiourea-formaldehyde condensa-

<sup>33</sup> L. Smidth, U. S. P. 1,704,348, Mar. 5, 1929, to E. G. Budd Mfg. Co.; *Chem. Abs.*, 1929, 23, 2000. British P. 294,254, 1928; *Brit. Chem. Abs. B.*, 1930, 338.

<sup>34</sup> G. L. Kelley and M. W. Deisley, British P. 319,687, 1928, to E. G. Budd Mfg. Co.; *Chem. Abs.*, 1930, 24, 2559. French P. 681,831, 1929; *Chem. Abs.*, 1930, 24, 4363. Canadian P. 315,214, 1931, *Chem. Abs.*, 1932, 26, 1730.

<sup>35</sup> R. W. Belfit, Canadian P. 349,461, 1935, to Scovill Mfg. Co.; *Chem. Abs.*, 1935, 29, 4106.

<sup>36</sup> W. S. Rothera, S. Blythen and H. R. Gillespie, German P. 553,502, 1930; *Chem. Abs.*, 1932, 26, 6166.

<sup>37</sup> G. H. Mains, U. S. P. 1,901,056, Feb. 12, 1935, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1935, 29, 2384.

<sup>38</sup> G. H. Gardner, British P. 413,727, 1934, to The Bushing Co., Ltd.; *Chem. Abs.*, 1935, 29, 531.

<sup>39</sup> British P. 374,914, 1931, to H. Rommler A.-G.; *Brit. Chem. Abs. B.*, 1932, 808. French P. 716,189, 1931; *Chem. Abs.*, 1932, 26, 2334. German P. 593,563, 1933; *Chem. Abs.*, 1934, 28, 1153.

<sup>40</sup> British P. 345,935, 1929, to Toledo Scale Mfg. Co.; *Chem. Abs.*, 1932, 26, 2025.

<sup>41</sup> J. F. Sisley, *Rev. gén. mat. color.*, 1932, 36, 334; *Brit. Chem. Abs. B.*, 1932, 978. French P. 713,283, 1930, to Soc. anon. des mat. color. et prod. chim. de Saint-Denis; *Chem. Abs.*, 1932, 26, 1800.

<sup>42</sup> K. Eisenmann and J. Kuchenbuch, German P. 524,686, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3752.

tion products for use in resin formation. The condensation takes place in the presence of organic solvents (ethyl alcohol or acetone). As an example of the procedure,<sup>42</sup> 130 parts of trioxymethylene are dissolved in 320 parts of methyl alcohol and 18 parts of 50 per cent potassium hydroxide solution. Thiourea (152 parts) and an additional 18 parts of the potassium hydroxide solution are then added. After a short time, dimethylolthiourea, which can be solidified by washing with acetone, separates. A mixture of 136 parts of the dimethylolthiourea and 120 parts of dimethylolurea is suspended in 500 parts of methyl alcohol. While stirring, 5 parts of sodium tetroxalate are added, and the mixture is heated to gentle boiling for 1 hour. The clear, viscous solution is neutralized and filtered. This product, mixed with various other resins, cellulose esters or cellulose ethers, can be used in lacquer manufacture. By evaporating the solvent *in vacuo* from the solution, a viscous material, that forms a resin with good electrical properties after heat treatment, is obtained.

Ripper<sup>43</sup> produced molding compositions by condensing thiourea, or a mixture of thiourea and urea containing not less than 1 mol of the former per mol of urea, in boiling aqueous solution with formaldehyde. Not more than 3 mols of formaldehyde per mol of thiourea are used, or if the mixed ureas are employed, 2 mols of formaldehyde are added for each mol of urea and thiourea. Contact with cold water converts the resinous products to a fine powder that may be hot-pressed. Opaque final products are formed when the urea and thiourea are condensed simultaneously, whereas clear resins are given by initiating the reaction with thiourea before adding a solution of urea in formaldehyde.

In forming condensation products of urea, thiourea and formaldehyde, von Knilling<sup>44a</sup> proposed to carry out the reaction by fusion. In one example an intimate mixture of 200 parts of urea, 52 parts of thiourea, 240 parts of trioxymethylene, 6 parts of sodium acetate and 20 parts of formamide is heated at 140°C. for 20 minutes. A viscous melt is formed which on cooling becomes a hard white mass that may be powdered for use in moldings or adhesives.

Molding powders were made by Ripper<sup>44</sup> by heating aqueous formaldehyde with thiourea, alone, until a hydrophobe resin, which separated from a sample of the reaction mixture on cooling, had formed. On adding water, the condensation product was precipitated as a fine powder, which was separated, washed and dried. Bussard<sup>45</sup> also described the condensation of thiourea with aqueous formaldehyde, using an acid catalyst (e.g., acetic acid). Neuss<sup>46</sup> sought to improve the flow of the product obtained by the acid condensation of formaldehyde and urea without heat, by substituting thiourea for 10-20 per cent of the urea. Starch, in an amount equal to a multiple of the quantity of urea employed, is used as has been noted before as a filler in the condensation of urea or thiourea with formaldehyde.<sup>47</sup> Kappeler<sup>48</sup> described the preparation of a resin from thiourea and furfural. The thiourea is dissolved in dilute hydrochloric acid and furfural added. The mixture becomes warm and a hard black mass forms. The formation of resinous substances in the condensation of nitriles with thioamides was reported by Ishikawa.<sup>49</sup>

In an investigation of the reaction between aryl thioureas and both aliphatic and aromatic aldehydes, Schmidt<sup>50</sup> obtained several species of resins. Thus, di-*o*-tolyl-thiourea (1 mol) is condensed with 2 mols of aqueous formaldehyde by re-

<sup>42</sup> British P. 319,251, 1928, addn. to 261,029, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.* 1929, 1047.

<sup>43</sup> K. Ripper, British P. 287,568, 1928; *Brit. Chem. Abs. B.* 1929, 863.

<sup>44a</sup> W. von Knilling, U. S. P. 1,920,451, Aug. 1, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4890.

<sup>44</sup> K. Ripper, U. S. P. 1,899,109, Feb. 23, 1933; *Chem. Abs.*, 1933, 27, 2771.

<sup>45</sup> C. Bussard, French P. 667,832, 1929; *Chem. Abs.*, 1930, 24, 1476.

<sup>46</sup> O. Neuss, British P. 408,869, 1932; *Brit. Chem. Abs. B.* 1934, 511.

<sup>47</sup> I. Thorn, British P. 287,727, 1927, to Silur Techn. & Chem. Prod. G.m.b.H.; *Brit. Chem. Abs. B.* 1928, 419.

<sup>48</sup> H. Kappeler, Swiss P. 123,387, 1927; *Chem. Abs.*, 1930, 24, 476. See also Chapter 24.

<sup>49</sup> S. Ishikawa, *Sci. Papers Inst. Chem. Research (Tokyo)*, 1927, 7, 237; *Chem. Abs.*, 1928, 22, 1581.

<sup>50</sup> J. G. Schmidt, U. S. P. 1,919,135, July 18, 1933, to E. F. Houghton & Co.; *Chem. Abs.*, 1933, 27, 4814. I. M. Lipovskii (Russian P. 33,300, 1933; *Chem. Abs.*, 1934, 28, 8606) prepared plastic masses from diphenylthiourea and formaldehyde. R. F. Hunter (J.C.S., 1926, 2956) obtained an orange-red resin by treating phenylisocyanthiocarbamide with bromine in chloroform solution. *p*-Phenylisobutylthiocarbamide gave a red gum which changed to a crystalline mass, but resinified on treatment with ether.

fluxing, and an oil, which on continued heating forms a resin fusing at 50°C., separates. Organic solvents may replace water as the reaction medium. Benzaldehyde and di-o-tolyl-thiourea give a stable, whitish reaction product (m.p. 160-177°C.) that is soluble in ether, alcohol, benzene, chloroform, acetone and carbon disulphide, but not in water. A product<sup>52</sup> of viscous, or resinous, character may be prepared by heating ethylene or butylene glycol with thiourea. The latter is then boiled with formaldehyde under reflux. The thiourea can be replaced wholly or in part by urea, and other agents such as acetylaniline, cyclohexanone, benzylglycol and crotonaldehyde used instead of formaldehyde.

### THIOCYANATE COMPOSITIONS

As stated in the section on the production of thiourea, ammonium thiocyanate rearranges under the influence of heat to form thiourea. The conversion, however, is not complete; and, at 170°C., equilibrium is reached in about 1 hour, giving a mixture containing 25 per cent of thiourea.<sup>53</sup> Several investigators have prepared resins directly from formaldehyde and ammonium thiocyanate, others have used thiocyanates in conjunction with urea- or thiourea-formaldehyde condensations.

Ammonium thiocyanate combines with formaldehyde in concentrated aqueous solution in equimolecular proportions without production of carbon dioxide. The condensation product can combine with further quantities of formaldehyde, forming bodies which, however, are less stable and readily part with some formaldehyde. The products are amorphous yellow compounds without definite melting points and are practically insoluble except in strong acids and strong alkalies, which presumably decompose them into their components.<sup>54</sup>

Experiments conducted in the author's laboratory with ammonium thiocyanate and formaldehyde indicated a harder resin could be obtained by using formaldehyde in excess of equimolecular proportions. Ammonium thiocyanate was dissolved in the minimum amount of water required to put it into solution and admixed with aqueous 40 per cent formaldehyde solution, using equimolecular proportions. The mixture was heated to about 50°C. and the yellow solution became turbid. Then, a yellow resin precipitated. Water was poured off and the product was dried at 110°C. for several hours. When hot it was a yellow viscous liquid which solidified on cooling to an opaque light yellow mass. It was brittle and possessed a disagreeable odor. The resin was insoluble in alcohol, benzol, acetone and mixtures of these, either hot or cold. It was also insoluble in water. In aniline and phenol the resin dissolved and could be precipitated by adding alcohol or benzol. When two molecular proportions of formaldehyde were used the reaction progressed spontaneously after being started by gentle heating. The conversion proceeded with rising temperature and a hard amorphous precipitate formed and settled. This was collected and dried. It was found to be soluble in cresol on slight heating although there were some signs of decomposition. The odor of both of these resins when heated is very disagreeable.

Jacobson<sup>54</sup> prepared an acetone-soluble product that was compatible with nitro-

<sup>52</sup> M. Paquin, U. S. P. 1,986,067, Jan. 1, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1180.

<sup>53</sup> J. E. Reynolds, *Ann.*, 1896, 150, 224. J. E. Reynolds and E. A. Weiner, *J.C.S.*, 1903, 83, 1. A. Findlay, *ibid.*, 1904, 85, 408.

<sup>54</sup> Schmerda, *Z. angew. Chem.*, 1917, 30, 176; *J.S.C.I.*, 1917, 36, 942.

<sup>55</sup> R. A. Jacobson, U. S. P. 1,945,316, Jan. 30, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 2480. See also British P. 348,420, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 2070. L. H. Englund (U. S. P. 1,926,766, Sept. 12, 1933, to Victor Chemical Works; *Chem. Abs.*, 1933, 27, 5712) used ammonium thiocyanate in coating compositions designed to prevent the rusting of metal surfaces. E. Söderbäck (*Ann.*, 1928, 465, 184; *Brit. Chem. Abs. A*, 1928, 1229) found that an aqueous solution of sodium hydroxytetrahydrothiocyanate gels even at a 0.02 molar concentration.

cellulose by heating ammonium thiocyanate and formaldehyde. A solution containing 60 g. of ammonium thiocyanate, 360 g. of 37 per cent formalin and 15 cc. of 10 per cent hydrochloric acid is refluxed for 1-2 hours and then concentrated to about 145 g. A yellowish syrup is formed, insoluble in water and alcohol, but soluble in acetone. The acetone-soluble material may be incorporated with nitrocellulose to form coating compositions, or it may be rendered insoluble by heating at 100-110°C. for 6-8 hours. A composition containing casein, ammonium thiocyanate and paraformaldehyde was used by Pierson<sup>55</sup> as an adhesive in wood-working.

On refluxing 1 mol of ammonium thiocyanate with 1.5-2 mols of aqueous formaldehyde, a resin is formed that may be dried, powdered and molded.<sup>56</sup> The excess of formaldehyde is condensed with urea, thiourea or resorcinol, added just before the molding operation; and an alkyd resin is added as a plasticizer. Free sulphur usually separates in the initial condensation, but this is allowed to remain and functions as a filler. The molding powder is stable and can be stored.

Gams and Widmer<sup>57</sup> prepared a resin solution by boiling, in a neutral medium, 600 parts by weight (1 mol) of urea with 1500 parts by volume (2 mols) of 40 per cent formalin. To 200 parts of this solution, 30 parts by volume of a 10 per cent ammonium thiocyanate solution are added, and the mixture is poured into molds. After a few minutes the mass gelatinizes and hardens to a snow-white product (sp. gr. 0.8-0.9) on standing. Cellulosic textiles may be impregnated with soluble condensation products of formaldehyde and ammonium thiocyanate or ammonium sulphide in the presence of urea.<sup>58</sup> The treated material is dried and heated to complete the polymerization of the impregnant.

The addition of metal thiocyanates to urea-formaldehyde molding compositions is said to promote polymerization in the hot-press and improve the moldings.<sup>59</sup> Urea, aluminum thiocyanate and formaldehyde are heated together in the presence of an alkali, giving a mucilaginous precipitate. The incorporation of the condensation product of a metallic thiocyanate and formaldehyde with a urea-aldehyde reaction mixture has also been used in preparing a molding resin.<sup>60</sup> If acid salts are added to an evaporated reaction product of calcium thiocyanate, thiourea and formaldehyde, a yellow resin is precipitated.

<sup>55</sup> G. G. Pierson, U. S. P. 1,964,960, July 3, 1934, to Perkins Glue Co.; *Chem. Abs.*, 1934, 28, 5192.

<sup>56</sup> A. M. Howald, U. S. P. 1,910,338, May 23, 1933, to Toledo Synthetic Products, Inc.; *Chem. Abs.*, 1933, 27, 4110.

<sup>57</sup> A. Gams and G. Widmer, U. S. P. 1,831,706, Nov. 10, 1931, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 815.

<sup>58</sup> French P. 753,559, 1933, to Résines et vernis artificiels; *Chem. Abs.*, 1934, 28, 1202. British P. 424,535, 1934; *Brit. Chem. Abs. B.*, 1935, 450.

<sup>59</sup> British P. 364,069, 1929, to Pfenning-Schumacher-Werke G.m.b.H.; *Chem. Abs.*, 1933, 27, 1724.

<sup>60</sup> British P. 364,068, 1929, to Pfenning-Schumacher-Werke G.m.b.H.; *Chem. Abs.*, 1933, 27, 1724.

## Chapter 32

### Modified Urea Resins. Resins from Urea Derivatives

As a class the resins made from urea and formaldehyde lack flexibility when hardened and for the most part are only sparingly soluble in organic solvents. In view of this, many suggestions have arisen concerning the problem of conferring greater toughness and flexibility on these resins by incorporation of other types. In some cases, no doubt, these added resins react with the urea resin group to form a complex. Since both urea and phenol react with formaldehyde, there have been numerous suggestions on methods of making composite resins in which a phenolic condensation product is a constituent. This has one disadvantage, namely, that although the urea resins are light-stable, the phenolic resins as a class are discolored on standing exposed to light. Other resins, therefore, have been tested, including the alkyd resins, which as a group are more stable to light than the phenolic resins. In addition there is a multiplicity of suggestions for use of various other resins, some of which are too costly to be utilized for the purpose and others have disadvantages of one sort or another. Since urea has been made on a large scale for fertilizer purposes, its low price in consequence makes possible the production of molding compositions at a cost comparable in a large measure with those made from phenolic bodies. Any addition, therefore, which tends to increase the cost to a considerable extent is barred for this reason. Likewise resins intended for use in lacquers should be made at a cost comparable with other lacquer resins of equivalent properties. These points should not be overlooked in the study of commercially available products.

#### UREA-ALDEHYDE RESINS WITH PHTHALIC ACID-GLYCEROL RESINS

Hill and Walker<sup>1</sup> averred that chemical combination occurred on mixing the two varieties of resin. Even a small proportion (5 per cent) of the urea-formaldehyde product produces in an alkyd resin a larger effect than they could account for by the formation of a physical mixture. The selection of the alkyd resin is determined by the purpose for which the final product is intended. If hardness is the only requisite, a straight glycerol-phthalic anhydride resin should be employed. The use of castor oil-alkyd products leads to stock intended for making flexible and light-colored lacquers. To make resins compatible with nitrocellulose esters, the proportions of the two types must be properly adjusted (in this case 70 parts of alkyd resin are used per 30 parts of dimethylolurea). Drying oils or drying oil acids are stated not to effect the hardenability of the resin mixture, but their use is detrimental to the color of the product.

The acidity of the reacting alkyd resin requires regulation and must not be too marked; although a small amount of acid serves as a hardening catalyst. Lacquers made with a resin containing upwards of 0.05 per cent of acid harden at room temperature, and similarly acid-catalyzed compound resins admixed with cellu-

<sup>1</sup> R. Hill and E. E. Walker, U. S. P. 1,877,130, Sept. 13, 1932; *Chem. Abs.*, 1933, 27, 200. British P. 344,401, 1929, to Imperial Chemical Industries, Ltd.; *Brit. Chem. Abs. B*, 1931, 597. French P. 694,181, 1930; *Chem. Abs.*, 1931, 25, 2013.

lose derivatives give films that are reported to become insoluble rapidly at ordinary temperatures. The acid catalysts used include sulphuric acid, hydrochloric acid, p-toluene sulphonic chloride, trichloroacetic acid and boric acid. Mixing of the two kinds of resin is performed in a solvent (ethylene chlorohydrin, dichlorohydrin, glycol monoethyl ether, butyl alcohol or cyclohexanol).

As an example of the method, 148 parts of phthalic anhydride, 62 parts of glycerol and 150 parts of castor oil are heated at 190-200°C. for 3-4 hours, while a current of carbon dioxide or nitrogen is passed through the reaction mixture. The resulting resin is a tough, flexible, moderately hard substance that is soluble in ketones, esters, hydrocarbons and hot alcoholic solvents. A solution of 14 parts of this resin in 14 parts of butyl alcohol is prepared, and the  $p_H$  of the liquid is adjusted to 6. Next, 3 parts of urea are added, heat being applied to complete solution, and 3 parts of para-formaldehyde are introduced into the hot mixture. After refluxing for the completion of the aldehyde reaction, the solution is diluted with 10 parts of solvent naphtha and filtered to remove suspended matter. The resulting lacquer gives transparent, colorless coatings after baking. The resin itself, which is compatible with nitrocellulose, may be isolated by solvent-evaporation *in vacuo* at low temperatures. Brown lacquers are obtained when linseed oil fatty acids are added to the resin composition.

If 100 parts of the prepared alkyd resin are dissolved in 200 parts of glycol monoethyl ether with 100 parts of dimethylolurea, reaction occurs on refluxing for a half hour. Methylated spirits (85 parts) and toluene (85 parts) are added, and the lacquer is clarified by filtration. The addition of this lacquer to a nitrocellulose solution containing small amounts of sulphuric acid gives a coating composition that dries in slightly over one hour at room temperature after application. The acids already mentioned confer on these resins the property of hardening in the cold.

To save the cost of expensive solvents, polyhydric alcohol-polybasic acids may be used as aqueous emulsions for coating purposes, and urea-formaldehyde resins can be incorporated with effects resembling those produced when solvents are employed.<sup>3</sup>

Thus, 8 parts of a urea-formaldehyde resin (prepared from 2 mols of formaldehyde and 1 mol of urea with boric acid as a catalyst) and 0.25 part of ammonia are mixed with 95 parts of water. Then, 40 parts of an alkyd resin, prepared by heating 31 parts of glycerol, 74 parts of phthalic anhydride and 75 parts of castor oil for 3-4 hours at 190-200°C., are dissolved in 32 parts of solvent naphtha and 28 parts of butyl alcohol with 4 parts of oleic acid. The two solutions are vigorously mixed, forming an emulsion that may be applied to material (e.g., rubber or leather cloth) and is hardened by heating at 115°C. for 2 hours.

Goldschmidt and Mayrhofer<sup>2</sup> recommended the addition of the liquid or viscous product obtained from phthalic anhydride and polyhydric alcohols to an aqueous mixture of urea and formaldehyde. The addition may be made prior to, during or after an alkaline or acid condensation. The ratio of urea to phthalic anhydride must be considerably greater than 1. Transparent, vitreous products, that can be hardened in molds without cracking at a higher temperature than normally, are obtained. Synthetic resins of this class were also studied by Jaeger.<sup>4</sup> Although less readily obtainable compounds will give much the same results, glycerol and glycol are the most important polyhydric alcohols used, and phthalic anhydride is the principal acidic ingredient. A large variety of monocarboxylic acids (including abietic acid, cinnamic acid, linolenic acid, rape oil acids, stearic acid, whale oil acids and furoic acid) and the usual plasticizers and fillers may be incorporated in the

<sup>3</sup> W. Baird, British P. 349,983 and 349,464, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 2671.

<sup>2</sup> S. Goldschmidt and R. Mayrhofer, British P. 316,144, 1928; *Chem. Abs.*, 1930, 24, 1711. German P. 572,367, 1923; *Chem. Abs.*, 1925, 27, 3044.

<sup>4</sup> A. O. Jaeger, U. S. P. 1,890,093, May 24, 1932, to Selden Co.; *Chem. Abs.*, 1932, 26, 3945. U. S. P. 1,941,474, Jan. 2, 1934; *Chem. Abs.*, 1934, 28, 1890.

resins. In an example of Jaeger's method of making a powder for molding tableware, a resin is first prepared by heating 1 mol of phthalic anhydride, 1 mol of glycerol, 0.5 mol of phthalide and 0.5 mol of benzoic acid at 180-210°C. From 1.5 to 2 parts of this resin are mixed with 1 part of a urea- or thiourea-formaldehyde condensation product and a small amount (2-6 per cent) of a plasticizer (toluene sulphonamide). The composite resin is then ground with cotton flock or wood flour to form the molding powder. The molded article is milky-white and is said to be less brittle than exclusively urea-formaldehyde products. A phenol may also be used in preparing these resins.<sup>5</sup>

Ellis<sup>6</sup> has shown that phthalic acid, alone, is capable of acting as a catalyst in urea-formaldehyde condensations carried out at, e.g., superatmospheric pressures. Lougovoy<sup>7</sup> examined the effect of a large number of organic acids on this reaction. It appears that phthalic acid actually combines to a large extent in the resin, which contains little free acid unless a large excess is used initially. Such a resin is readily formed by refluxing 50 parts of urea, 50 parts of phthalic anhydride and 150 parts of aqueous formaldehyde and then evaporating. The products range from syrups, that are miscible with alcohols or ketones and are useful as varnishes and impregnating agents, to glassy solids. The solid products can be molded with fillers and can also be applied to the making of glass substitutes.

By fusing urea with phthalic anhydride and then reacting the product with formaldehyde, Bitterich<sup>8</sup> obtained a clear resin which could be molded or dissolved to form a varnish. As an example, 50 kg. of phthalic anhydride and 40 kg. of urea are fused and held molten for a time at 200°C. After cooling the mass to 80°C., 80 kg. of 40 per cent formalin are added and the reaction is completed by heating for a half hour at 110°C. Water may be removed by distillation *in vacuo*. Acid catalysts may be employed and the fusion can be carried out in a high-boiling solvent.

A glycerol ester of phthalic acid may be fused and mixed with lithopone, sawdust, urea and paraformaldehyde, forming a mass that is brittle when cold.<sup>9</sup> After disintegration, the composition is hot-pressed.

#### RESINS FROM UREA WITH ALCOHOLS OR KETONES

Urea and other organic amines were employed by Burke<sup>10</sup> as accelerators of the polymerization of ketone-formaldehyde condensation products (see Chapter 25) in conjunction with fillers and other modifiers. The products are used with pyroxylin for coating compositions.

Paquin's investigations<sup>11</sup> in this field concerned the condensation products of urea and thiourea (or their derivatives) with alcohols or ketones, many of which condensates were capable of further reaction with aldehydes. Urea and its derivatives normally condense with alcohols or ketones to form well-defined crystalline substances, but prolonged interaction was found to give oily or resinous products.<sup>12</sup> Other amino compounds may be employed in the condensation, but in any case the resulting products react further with aldehydes. By heating 139 parts of ethyl alcohol and 60 parts of urea for 5 hours at 180-190°C. under pressure, an oil is

<sup>5</sup> German P. 526,169, 1927, to Jaroslaw's Erste Glimmwaren-Fabrik; *Chem. Abs.*, 1931, 25, 4422.

<sup>6</sup> Carleton Ellis, U. S. P. 1,897,978, Feb. 14, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 2831. See also Carleton Ellis, U. S. P. 2,009,545, July 30, 1935.

<sup>7</sup> B. N. Lougovoy, U. S. P. 1,756,251, Apr. 20, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1930, 24, 3122. For use of phthalic acid, salicylic acid and oxalic acid, see French P. 711,367, 1931, to Brit. Cyanides Co., Ltd.; *Chem. Abs.*, 1932, 26, 1813.

<sup>8</sup> F. Bitterich, U. S. P. 1,971,476, Aug. 28, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 6580.

<sup>9</sup> British P. 318,883, 1929, to Bakelite G.m.b.H.; *Brit. Chem. Abs. B*, 1930, 997.

<sup>10</sup> C. E. Burke, U. S. P. 1,755,099, Apr. 15, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 24, 2905.

<sup>11</sup> M. Paquin, U. S. P. 1,924,253, Aug. 29, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5402.

<sup>12</sup> M. Paquin, U. S. P. 1,902,859, Mar. 28, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3300. German P. 806,968, 1926; *Chem. Abs.*, 1931, 25, 838. British P. 278,890, 1926; *Chem. Abs.*, 1928, 22, 2673. French P. 641,770, 1927; *Chem. Abs.*, 1929, 23, 1237. British P. 360,909, 1931.

formed. The oil is separated from its content of urethan and allophanic esters by vacuum distillation and is soluble in water and organic solvents. Urea (60 parts), benzyl alcohol (200 parts) and glycerol (6 parts) form a similar, viscous oil, soluble in organic solvents. A water-soluble oil, that is purified by fractional distillation, is prepared also by heating 240 parts of ethylene glycol and 96 parts of thiourea for 1.5 hours at 190-200°C. A light-yellow resin is obtained by refluxing 327 parts of cyclohexanone and 200 parts of urea for 1.25 hours in an apparatus heated with water at 90°C. The clear resin (100 parts) may be further



*Courtesy Bakelite Corp.*

FIG. 112.—A Rotary Preforming Machine which Compresses Tablets into Proper Shape for Molding.

refluxed with 70 parts of 35 per cent formaldehyde, yielding a limpid product after expelling water. Toluene sulphonamide is also used in these reactions.<sup>13</sup>

Metals react with these products, giving substances with high viscosities and improved solubility in water.<sup>14</sup> Thus, 180 parts of butylene glycol are heated in a reflux apparatus with 80 parts of urea and 5 parts of metallic calcium. Hydrogen is evolved and, after 45 minutes, a yellow, viscous oil is obtained. Zinc, cadmium and similar metals, introduced during or after the completion of the reaction between the urea and the alcohol or ketone, are also dissolved with evolution of hydrogen. These oils and resins are useful as softening agents for casein and gelatin.

<sup>13</sup> M. Paquin, German P. 508,796, 1927, addn. to 506,963, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 835. British P. 287,095, 1927; *Chem. Abs.*, 1929, 23, 533.

<sup>14</sup> M. Paquin, German P. 510,428, 1927, addn. to 506,963, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1400. German P. 512,831, 1927, addn. to 510,428; *Chem. Abs.*, 1931, 25, 1400. British P. 290,192, 1928, addn. to 278,890; *Brit. Chem. Abs. B*, 1929, 709.



The urea-alcohol or ketone reaction requires no external heat when allowed to take place in the presence of strong mineral acids.<sup>15</sup> As an example, 192 parts of 1,3-butyleneglycol are mixed with 120 parts of urea and 8 parts of concentrated sulphuric acid. During this operation, the temperature gradually rises to 40-60°C. and a clear solution is obtained. After stirring for 5 hours, a viscous, oily product is formed, which is freed from acid and purified by vacuum distillation. The condensation products of urea or its derivatives with an alcohol or ketone improve the dispersion of dyes in dye pastes and printing compositions and prevent the formation of crusts.<sup>16</sup>

The formation of resins (as opposed to oily products) in this group of reactions depends on length of heating or on the presence of an aldehyde (notably formaldehyde). Prolonged heating will probably convert any of the oils mentioned to resins, but this result is achieved more readily by the use of aldehydes. Thus, butylene glycol, urea and formaldehyde give a clear, resinous mass when heated together.<sup>17</sup> If a low temperature is employed, the products are generally soluble in water or alcohols.

Paquin<sup>18</sup> described a lacquer composed of bronze powder mixed with a vehicle obtained by reacting urea with a cyclic acetal derived from glycerol and acetaldehyde.

Urea or its derivatives will also condense with polyvinyl alcohol and other highly polymerized alcohols.<sup>19</sup> The polyvinyl alcohol may be condensed with an aldehyde (formaldehyde) and simultaneously or subsequently reacted with phenol, urea or aniline.<sup>20</sup> Alternatively, the alcohol is condensed with a methylol compound (urea-formaldehyde or phenol-formaldehyde). The products are useful for sizes, emulsions or molded articles.

The two-stage, urea-formaldehyde process (see Chapter 27), wherein methylol-urea is first isolated, renders it possible to obtain resins of modified properties. Thus, by heating methylolurea (or methylolthiourea) or its polymers with a compound containing at least 2 free hydroxyl groups, water-soluble resins are obtained.<sup>21</sup> Such products, best condensed by acid in the presence of a buffer, serve as sources of artificial horn or casein.<sup>22</sup>

Alternatively, the urea-formaldehyde condensation may be performed in the presence of excess of a compound containing at least 1 free hydroxyl group and another reactive group (the amino or carboxyl group). The later reaction of this additional group can be used to modify the product. Pungs, Eisenmann, Scholz and Kollmann<sup>23</sup> have investigated the production and utilization of these modified types. The additional group in the condensate may be reacted with organic compounds capable of forming an oxygenated linkage (alcoholates, phenols, phenolates, alkylene oxides and acid chlorides or anhydrides). The reagents containing one or more hydroxyl groups and an additional reactive group include ethylene chlorohydrin, glycerol  $\alpha$ -monochlorohydrin or  $\alpha,\beta$ -dichlorohydrin and esters of polyhydric alcohols with polybasic organic acids, as, e.g., esters of phthalic acid, oxalic acid, succinic acid, adipic acid or tartaric acid of the type

<sup>15</sup> M. Paquin, German P. 508,795, 1926, addn. to 506,963, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 835. British P. 280,238, 1926; *Chem. Abs.*, 1928, 22, 3056.

<sup>16</sup> British P. 318,178, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2307.

<sup>17</sup> M. Paquin, German P. 523,912, 1927, addn. to 506,963, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3856. British P. 292,595, 1927; *Chem. Abs.*, 1929, 23, 1518.

<sup>18</sup> M. Paquin, German P. 529,990, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 5305.

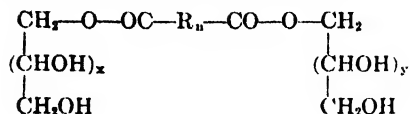
<sup>19</sup> German P. 519,049, 1930, addn. to 506,963, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3782.

<sup>20</sup> A. Voss, German P. 542,286, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2286. French P. 700,411, 1930; *Chem. Abs.*, 1931, 25, 3782.

<sup>21</sup> British P. 320,815, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2623.

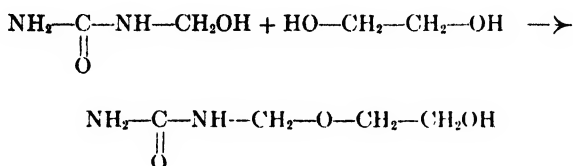
<sup>22</sup> French P. 651,086, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 3315.

<sup>23</sup> W. Pungs, K. Eisenmann, E. Scholz and T. Kollmann, U. S. P. 1,963,762, June 19, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3263. German P. 540,071, 1929; *Chem. Abs.*, 1932, 26, 1812. British P. 360,909, 1930; *Chem. Abs.*, 1933, 27, 1220. French P. 706,044, 1930; *Chem. Abs.*, 1932, 26, 267.

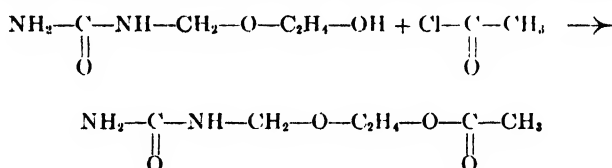


(in which R represents an aliphatic, cycloaliphatic or aromatic hydrocarbon radical, x and y are any whole numbers and n may be zero or a whole number) or esters of benzoic (or other monobasic aromatic or aliphatic, saturated or unsaturated acids) with polyhydric alcohols.

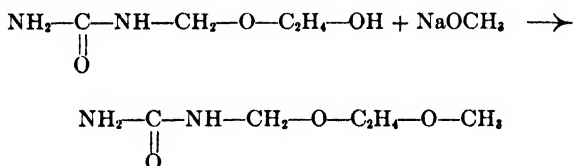
The condensation of monomethylolurea with glycol proceeds according to the scheme:



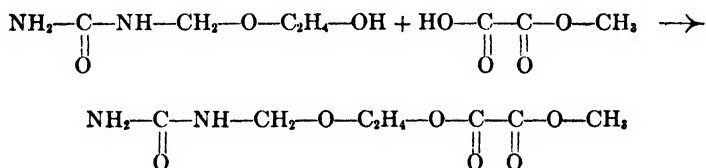
The resulting compound gives an ester on further reaction with acetyl chloride,



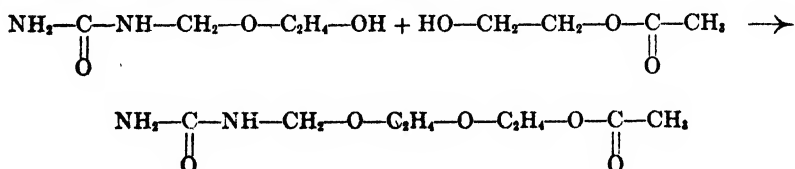
an ether with sodium methylate,



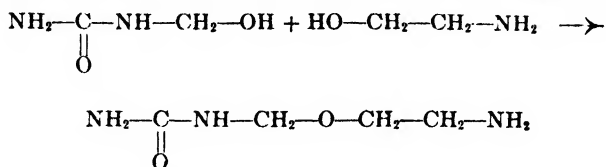
a diester with the acid methyl ester of oxalic acid,



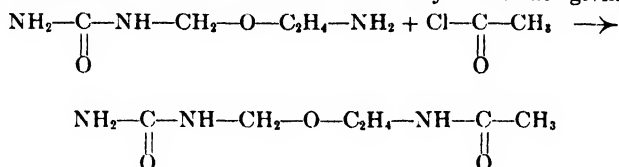
and an ester-ether with glycol monoacetate,



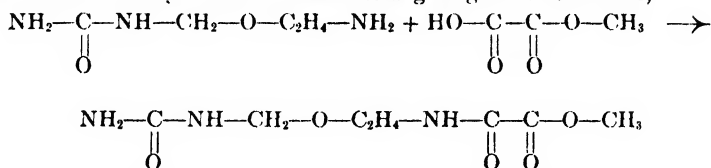
The reaction of monoethanolamine with monomethylolurea is as follows:



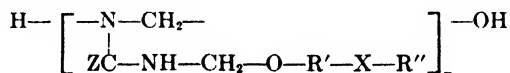
The substance obtained reacts further with acetyl chloride giving an amide,



and with the acid methyl ester of oxalic acid giving an ester-amide,



Similarly, a methylolurea may react with a hydroxy-carboxylic acid (HOR-COOH) with the formation of an ether or ester group. The remaining carboxyl or alcoholic group is then further reacted. In each case the products correspond to the general formula



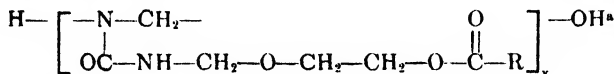
in which  $x$  is an integral number greater than 1,  $Z$  denotes oxygen or sulphur,  $\text{R}'$  indicates an alkyl radical (in which hydrogen atoms may be replaced by oxygen, ether or ester radicals) containing at least 2 carbon atoms and which is linked through  $\text{X}$  (an ether oxygen atom, a carboxyl group, an amine group or a carboxylic amide group) to a hydrocarbon radical,  $\text{R}''$ .

The reaction is usually performed with the halogen substitution products of the polyhydric alcohols, and the halogen content of the reaction products is determined to measure the amount of alcoholate or sodium salt necessary for the subsequent etherification or esterification. When used in excess, the reaction components serve as solvents. The separation of any excess can be carried out, before the conversion of the reactive groups in the primary products, by precipitation of the condensate or by steam distillation.

In an example outlined in the investigations of Pungs, Eisenmann, Scholz and Kollmann,<sup>24</sup> 80 cc. of a 5 per cent (by weight) ethyl alcohol solution of urea nitrate are added to 1200 g. of ethylene chlorohydrin at 95°C., 800 g. of dimethylolurea are then slowly introduced while stirring, and the whole is stirred for a further 20 minutes at 90°C. After cooling the solution, neutralizing with tertiary sodium phosphate and filtering, 5 times its volume of 95 per cent ethyl alcohol is added while stirring vigorously, the condensation product thus separating in a powdery form. The powder is washed with ether and dried *in vacuo* at 40-50°C. The substance contains 9 per cent of chlorine. The alcohol-precipitated product (250 g.) is dissolved in 600 g. of ethylene glycol monomethyl ether, and 200 g. of the sodium soap of linseed oil

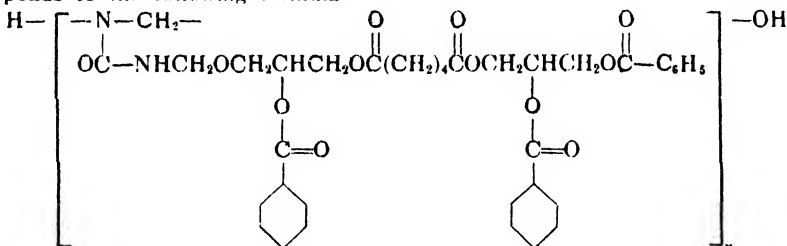
<sup>24</sup> *Loc. cit.* See also K. Eisenmann, E. Scholz and K. Wolf, German P. 588,426, 1933, to I. G. Farbenind. A.-G.; *Chem. Abn.*, 1934. 28. 1560.

fatty acids are added to the solution. The reaction mixture is then heated at 120°C. for 12 hours with stirring and separated from precipitated sodium chloride. The reaction, which is carried out with a quantity of sodium soap slightly exceeding that required for esterification, proceeds practically quantitatively. The small amount of soap still present is removed by careful neutralization with a few drops of glacial acetic acid, the linoleic acid set free being then dissolved in the ether. By mixing the solution with 5-6 times its volume of ethyl ether, the condensation product is precipitated. After repeated washing with ether and drying, a yellow-brown resin having an appearance similar to linoxyn is obtained. The resin probably corresponds to the formula:

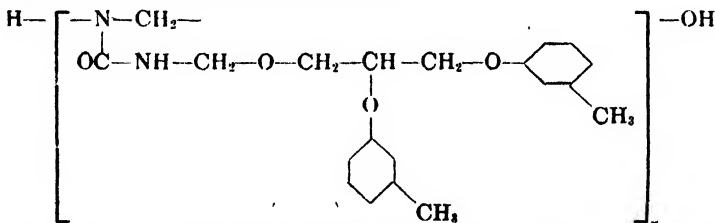


<sup>a</sup> R is the linseed oil radical.

In another example, 100 parts of adipic 1,1'-diglyceride (prepared by the reaction of the sodium salt of adipic acid with  $\alpha$ -monochlorohydrin) are diluted with 40 parts of dioxane, heated to 90°C. and treated with 0.7 part of concentrated hydrochloric acid, 50 parts of dimethylolurea being then added with stirring. After stirring for half an hour at 90°C., the reaction mixture is neutralized with tertiary sodium phosphate, and the condensation product is precipitated from the filtered and cooled solution by the admixture of 8 times its volume of 95 per cent ethyl alcohol. The dried, pulverized product (6 parts by weight) is suspended in 100 parts by weight of pyridine. To this suspension, 6 parts of benzoyl chloride are added, and the mixture is stirred while being cooled with ice until the reaction is complete. The reaction mixture is then poured into water; a pale-yellow oil separates and is washed with water. An ethylene glycol monomethyl ether solution of the oil leaves on a substratum after drying a colorless, firmly adherent film that may be hardened at elevated temperatures (100-120°C.). The product also possesses great adhesive power and probably corresponds to the following formula



In an additional example, 450 parts of glycerol are kneaded with 5 parts of oxalic acid and 900 parts of dimethylolurea and heated to 100°C. for 2 hours. The resulting, hard, white mass is pulverized in a mill, and 175 parts of the disintegrated substance are dissolved at 100°C. in 200 parts of distilled, commercial cresol.<sup>25</sup> After cooling to 80°C., 4.5 parts of phosphorus pentoxide are added with stirring, raising the temperature to 95°C. After 1 hour at 95°C., the resulting product, which is a tough, syrupy mass upon cooling, is washed with hot water (until the water remains neutral) and is freed from a remainder of cresol by treatment under diminished pressure with steam heated to 130°C. Water is removed by fusing *in vacuo* at 110°C., giving a clear, yellow resin which may be represented by the formula



<sup>25</sup> Pure m-cresol can be obtained from a mixture of cresols by treating with urea, separating the addition product and decomposing it with dilute mineral acids (French P. 660,091, 1928, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1930, 24, 130. British P. 297,083, 1928; *Brit. Chem. Abs.* B, 1929, 973).

The products of the various methods can be processed, by themselves or in admixture with substances including cellulose derivatives, natural or synthetic resins, softening agents, fillers and coloring materials, to form lacquers or plastic masses. An adhesive for abrasives may also be produced from the acid condensation of methylol derivatives of urea with hydroxylated esters of fatty acids, containing at least 10 carbon atoms, in the presence of a monohydric alcohol as solvent<sup>28</sup>. The resinous product, after a heat treatment at 80-130°C., is soluble in esters, ketones and aromatic hydrocarbons.

Luther<sup>27</sup> obtained clear, water-soluble masses by heating methylolureas with a polyhydric alcohol. A suspension of 500 parts of dimethylolurea in 700 parts of glycerol together with 20 parts of acid potassium oxalate are heated to 100-110°C. until a clear solution is obtained. If the solution is neutralized by means of an alkali-metal carbonate and filtered, a viscous product is formed which can be employed as a plasticizer for gelatin.

#### FURFURAL-UREA RESINS

Black, lustrous resins resembling ebonite are produced by the acid condensation of urea and furfural. Kappeler<sup>29</sup> prepared these resins by mixing 3 parts of urea (1 mol), 3 parts of 38 per cent hydrochloric acid and 1-3 parts of water with 5 parts of furfural (1 mol). The liquid becomes dark and is poured into molds, in which a lively reaction soon begins. The molds are cooled until the reaction moderates. When interaction ceases, the solid obtained is gradually heated to 100°C., giving the ebonite-like resin that is insoluble in the usual solvents, infusible and unaffected by alkalis or dilute acids. The resin becomes tougher on being baked with an impregnating agent (linseed oil). If alcohol, glycerol or acetone is substituted for water in the reaction, the resulting products possess a higher luster. The liquid mixture, prior to reaction, may be used for impregnating wood or cellulose.

A mixture of 3 parts of urea with 1 part of aniline, toluidine or other amine can be used to replace urea in the process. Aniline, p-toluidine, p-phenylenediamine and  $\alpha$ - and  $\beta$ -naphthylamine yield resins with furfural and urea.<sup>30</sup> Furfural may be replaced with a mixture of furfural and another aldehyde. Thus, a mixture of 4 parts of furfural and 2 parts of 40 per cent formaldehyde may be employed. The initial condensation of urea (3 parts) and furfural (5 parts) can be carried out at 100°C. in the absence of acid, giving a yellow resin that blackens and hardens on further heating with hydrochloric acid. Condensation of the reactants is also possible with 30 per cent sodium hydroxide solution. The product prepared in this manner is soft and soluble, but the black substance is again obtained when the condensation is completed with hydrochloric acid. In these reactions, furfural may also be replaced by furfuramide, and thiourea substituted for urea. Additions of coloring matter, sawdust, cork powder, leather powder, heavy spar, asbestos, glycerol, camphor, naphthalene, ketones, phenols and amines can be included in the resin composition.

In their investigations of urea-furfural resins, Novotny and Johnson<sup>30</sup> found that

<sup>28</sup> French P. 753,001, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 920. British P. 404,664, 1934; *Chem. Abs.*, 1934, 28, 4190.

<sup>27</sup> M. Luther, U. S. P. 1,905,937, Jan. 1, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1180.

<sup>29</sup> H. Kappeler, British P. 203,872, 1927; *Chem. Abs.*, 1929, 23, 1729. German P. 507,419, 1928. *Chem. Abs.*, 1931, 25, 566. Swiss P. 131,597, 1927; *Chem. Abs.*, 1929, 23, 5018. French P. 657,477, 1928; *Chem. Abs.*, 1929, 23, 4308.

<sup>30</sup> H. Kappeler, Swiss P. 133,713, 133,714, 133,715, 133,716, 133,717, 133,718, 1929, addns. to 131,597; *Chem. Abs.*, 1930, 24, 1711. See also Swiss P. 133,707 to 133,712 and 133,387, 1927, addns. to 131,597; *Chem. Abs.*, 1930, 24, 476.

<sup>30</sup> E. E. Novotny and W. W. Johnson, U. S. P. 1,827,824, Oct. 20, 1931, to J. S. Stokes; *Chem. Abs.*, 1932, 26, 862. U. S. P. 1,931,526, Mar. 20, 1934; *Chem. Abs.*, 1934, 28, 3606.

prolongation of condensation in the presence of hydrochloric acid gave products tending to become powdery and friable and that a small amount of a basic compound was a better catalyst for the reaction. With sodium carbonate or ammonia as catalyst, the condensation at 138°C. is readily controlled. Thus, a mixture composed of 100 lb. of urea, 300 lb. of furfural and 4 lb. of 26 per cent ammonia is refluxed at 104°C. for 2 hours, after which time the water and excess reactants are removed by distillation. During the distillation, the temperature should not exceed 158°C., or the substance will become hard and infusible. If overheating is avoided, the resulting resin is soluble in alcohol, acetone and ether, but insoluble in benzene and water. These soluble resins are useful as varnishes for impregnating paper, cloth and asbestos. After the solvents have been evaporated, the products are hot-molded to harden the resin, the hardening process being facilitated by formaldehyde. The hardened material possesses considerable mechanical strength and high dielectric properties.

Dry potassium or sodium carbonates, taken in quantities equivalent to 1 per cent of the total urea and furfural, are recommended by Novotny and Johnson to catalyze the reaction. A small amount (3 per cent) of a 20 per cent aqueous solution of potassium or sodium hydroxide may serve as a condensing agent.

Various modifying agents, including tung oil, lanolin and camphor can be added to the reacting mass. With 5 per cent of tung oil, the furfural-urea products have increased flexibility. A similar proportion of lanolin can be incorporated after the condensation reaction is completed and gives a resin intended for cold-punching.

#### ACROLEIN-UREA RESINS

Reaction between acrolein and urea occurs readily, its course depending on the relative proportions of the reactants, on the temperature and on the presence of catalysts, solvents or diluents. Gams and Widmer<sup>21</sup> made a study of the influence of the various conditions on the reaction. They found that if the proportions were 0.5 mol of aldehyde to one of urea, a highly viscous syrup could be obtained. With 0.75 mol of acrolein to 1 mol of urea, gelatinous substances are formed, and larger proportions of acrolein give vitreous, solid products. Without catalysts or solvents, the reaction is slow at ordinary temperatures, and it is best carried out in a closed vessel above the boiling point of acrolein (52°C.). The process occurs fairly quickly, even below 50°C., with a catalyst, and the reaction mixture must be cooled to prevent too violent an interaction. The catalysts used are inorganic or organic acids or bases, including sulphuric acid, acetic acid, sodium hydroxide solutions, ethylene diamine and acid or basic salts. Solvents, particularly when low temperatures are employed, advantageously facilitate the starting of the reaction, although the whole of the urea need not be dissolved. Water, methyl alcohol, ethyl alcohol and glycerol are employed as solvents or diluents and may be separated from the products at the conclusion of the reaction.

The urea-acrolein condensation can be performed in two stages. The first stage, using 0.5 mol of acrolein per mol of urea, yields the viscous, syrupy substance, which, in the second step, is converted to a gelatinous or hard material by merely adding additional acrolein. Formaldehyde can replace acrolein in the hardening process. Thiourea, methylurea and other urea derivatives can be sub-

<sup>21</sup> A. Gams and G. Widmer, U. S. P. 1,654,215, Dec. 27, 1927, to Soc. anon. pour. l'ind. chim. à Bâle; *Chem. Abs.*, 1928, 22, 849. German P. 554,552, 1925; *Chem. Abs.*, 1932, 26, 6081. British P. 280,288, 1925; *Chem. Abs.*, 1927, 21, 3432. See also C. Marx, *Plastics*, 1928, 4, 194.

stituted for the urea, and similarly acrolein itself can be replaced by acrolein polymers (disacryl or acrolein resins).

Specifically, if 12 parts of urea are heated with 11.2 parts of acrolein for about 1 hour at 100°C. in a closed vessel, a transparent, vitreous product results. On heating 12 parts of urea, 5.6 parts of acrolein and 0.03 part of glacial acetic acid for one hour at 80°C. in a closed container, a highly viscous, transparent mass is obtained. In another example, 60 parts of urea, 5 parts of water and 0.8 part of 1 per cent sulphuric acid are condensed with 56 parts of acrolein at 40-50°C. The resulting clear syrup is cooled for some hours and allowed to stand at ordinary temperatures until a solid jelly forms. In an example of the use of acrolein resins, 5 parts of a wax-white resin (made from acrolein by alkaline condensation) are condensed with 2 parts of urea at 100°C. A soft, yellowish resin is produced, and this can be hardened by further additions of urea.

The viscous syrups produced in these condensations serve as adhesives and varnishes. The hardened, vitreous products, because they are easily sawn, bored, cut, polished or shaved and are resistant to chemicals, are used for making all sorts of shaped objects. For special purposes, dyestuffs, fillers and agents imparting extra elasticity are added to the resins.

#### CONDENSATION WITH OTHER ALDEHYDES

The cost of formaldehyde and the instability (over long periods) of the initial condensation products were pointed out by Barsky and Wohnsiedler<sup>22</sup> as disadvantages of urea-formaldehyde resins. Hence, the investigators prepared a resin in which part of the formaldehyde was replaced by acetaldehyde. Thus, 300 parts of urea are dissolved in 510 parts of water, and 231 parts of acetaldehyde are added at 20-30°C. After adding 200 parts of 0.5 *N* hydrochloric acid, the mixture is allowed to stand for from several days to 1 week at 20-30°C. The resulting precipitate of ethylidene urea is filtered, and 22 parts of it are mixed with 30 parts of 38 per cent formaldehyde and 15 parts of water. A small quantity of 0.5 *N* hydrochloric acid (0.2 part) is introduced, and the mixture is boiled to effect solution. This solution gives a clear, water-soluble resin, if made alkaline with sodium hydroxide and concentrated; or it gives a water-insoluble product by means of concentration and a heat-hardening treatment at 70°C. An aqueous solution of the water-soluble resin is used to impregnate paper or fabric and is then made insoluble by an acid treatment.

The products can be cast or molded or incorporated with fillers to form molding powders. As an example, a mixture of 43 parts of ethylidene urea, 40 parts of 38 per cent formaldehyde, 25 parts of water and 2 parts of 0.5 *N* hydrochloric acid is refluxed and filtered. The clear syrup (94 parts) is incorporated with 27 parts of disintegrated paper pulp and dried to yield 75 parts by weight. When ground, this product forms a powder that can be molded at 145-160° under pressure.

The oxidation of petroleum hydrocarbons by air or an oxygen-containing gas furnishes a complex mixture of aldehydes which Ellis<sup>23</sup> used for direct combination with urea or thiourea. The aldehyde mixture is heated with urea for several hours until a syrupy liquid, useful as an impregnant, forms. Further heating transforms the syrup into a resin, but the latter is liable to have an acrid odor that should be removed by stronger heating or steaming.

Schmidt<sup>24</sup> described the use of aryl thioureas for reaction with formaldehyde,

<sup>22</sup> G. Barsky and H. P. Wohnsiedler, U. S. P. 1,896,276, Feb. 7, 1933, to American Cyanamid Co.; *Chem. Abs.*, 1933, 27, 2831.

<sup>23</sup> Carleton Ellis, U. S. P. 1,952,060, Mar. 27, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 3606.

<sup>24</sup> J. G. Schmidt, U. S. P. 1,919,135, July 18, 1933, to E. F. Houghton & Co.; *Chem. Abs.*, 1933, 27, 4814.

acetaldehyde and benzaldehyde to form resins (see Chapter 29). Wayne<sup>35</sup> prepared a water-soluble resin with emulsifying and wetting properties by condensing 1 mol of aldol with 1 mol of urea at 110-120°C.

#### PHENOLIC SUBSTANCES AS MODIFYING AGENTS

In a study of phenol-urea-formaldehyde condensations, Barthélemy<sup>36</sup> found that on the addition of aqueous alcohol to an alcoholic solution of the partially condensed product, a mixture of 2 colloidal suspensions is obtained. These suspensions can be separated into positive and negative components by the action of an electric field. The further condensation of the reactants depends on the nature of the catalytic ion and solvent employed and on the temperature.

Ellis<sup>37</sup> prepared an aldehyde-phenol-urea resin by first heating 210 parts of phenol and 150 parts of aqueous formaldehyde for 2 hours in an autoclave under a pressure of 100 lb. and at a temperature of 138-143°C. On completion of the reaction, water is removed, giving a fusible and alcohol-soluble resin. Well-dried dimethylolurea (1 part by weight) added to 10 parts of the phenolic resin raised the melting point of the latter substance. By adding increasing amounts of urea-formaldehyde condensation products, a range of molding powders can be obtained.

The fusible condensation product of furfural with excess of phenol in the presence of a small quantity of hydrochloric acid can be incorporated with varying amounts of dimethylolurea. Dimethylolurea was also found capable of incorporation with phenol-sulphur resins. As an example, 1 part of phenol is treated with 2-2.5 parts of sulphur monochloride, yielding a resin which is combined with 10 per cent or more of dimethylolurea. Additions of sulphur resins make the material more readily fusible and capable of flowing freely under combined heat and pressure, thus yielding a sharp impress during the molding operation.<sup>38</sup> A molding composition is also prepared by combining dimethylolurea with a phenol-furfural resin.

A light-stable, moldable product is made by condensing urea with a small amount of phenol and a large excess of formaldehyde.<sup>39</sup> After adding an excess of phenol and further amounts of formaldehyde, the mass is made alkaline, and water is distilled off *in vacuo* at 50°C. An organic acid (lactic acid) is added to neutralize the alkali, and the reaction water is removed *in vacuo* at 75°C. Lastly, the condensation product is molded and hardened at 80°C.

A condensation product of urea, formaldehyde and a phenol was prepared by Terwilliger<sup>40</sup> who found that it possessed greater water-resistance than urea resins. With an addition of only 5 per cent of phenol, the water absorption by a particular urea-formaldehyde resin was reduced to a half or less. Increase of phenol content raised the water-resistance, but 10 per cent of phenol was considered most efficient in this respect. Furthermore, the addition of phenol tended to reduce formaldehyde losses. In an example of the process, 40 parts by weight of urea are dissolved in 100 parts of a 40 per cent formaldehyde solution. The mixture is neutralized with ammonia, sodium hydroxide or calcium hydroxide until just acid to litmus, heated to 50°C. and filtered. The filtered solution is refluxed for 30 minutes and then evaporated until the initial boiling point of 97°C. is raised to 100-101°C., during which about 65 per cent of the water is removed. Phenol

<sup>35</sup> T. B. Wayne, U. S. P. 1,912,330, May 30, 1933; *Chem. Abs.*, 1933, 27, 4066.

<sup>36</sup> H. Barthélemy, *Chimie et industrie*, 1926, 16, 367; *Brit. Chem. Abs. B*, 1926, 955.

<sup>37</sup> Carleton Ellis, U. S. P. 1,536,881, May 5, 1925; *Chem. Abs.*, 1925, 19, 1956.

<sup>38</sup> Carleton Ellis, U. S. P. 1,897,978, Feb. 14, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 2831.

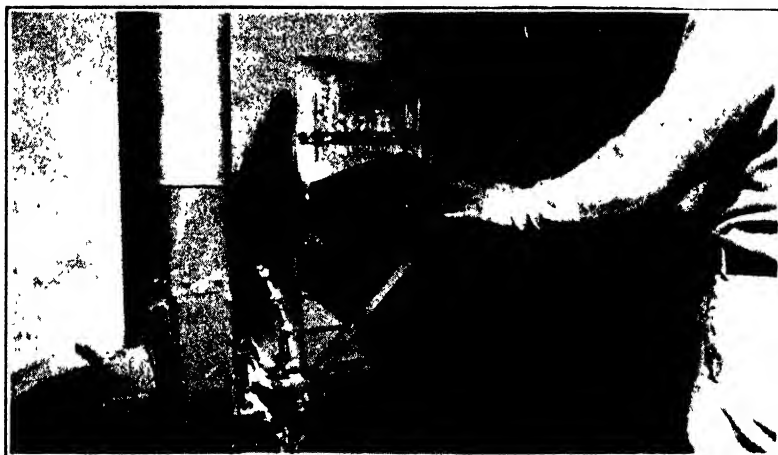
<sup>39</sup> German P. 557,549, 1927, to "Herold" A.-G.; *Chem. Abs.*, 1933, 27, 575.

<sup>40</sup> C. O. Terwilliger, U. S. P. 1,678,024, July 24, 1928, to F. v. Briesen; *Chem. Abs.*, 1928, 22, 3499.



(2 parts) is stirred into the hot solution which is then placed in a drying oven and kept at 75°C. for 2-3 hours, then at 85-95°C. for 4-5 hours and finally at 110°C. until hard.

Bender<sup>41</sup> prepared a resin by reacting a phenol with more than an equimolecular proportion of formaldehyde in the presence of a basic catalyst and by combining the excess aldehyde with urea or other resin-forming agents (thiourea or p-toluenesulphonamide) with the aid of an acid catalyst. In the method, 145 parts of phenol and 412 parts of 40 per cent formaldehyde solution are heated with 1-5 parts of sodium carbonate as catalyst. Water is separated by evaporation under reduced pressure, and most of the excess formaldehyde dissolves in the resin as paraform. Then, 40 parts of urea are added together with sufficient lactic acid or phosphoric acid to make the mass acidic. Heating is continued to complete the urea-formaldehyde reaction, and a solvent is added at this point



Courtesy Unytc Corporation

Fig. 113.—Paper-Shredding Machine Used in Preparing Fillers for Molding Compositions.

if a varnish or lacquer is the desired end product. The proportions used in the process should not be greater than 1 mol of urea for each 2 mols of residual paraform. The resins can be employed in the manufacture of transparent or colored articles, lacquers, enamels and white molding compounds. This type of resin was used by Lloyd<sup>42</sup> as a binder for mica sheets and tubes. Bender<sup>43</sup> also described the production of laminated products using these resins as binders or impregnating agents. The absence of any appreciable amount of free phenol or free formaldehyde in the binder gives the molded articles a light color. The odorless nature of these resins make them useful in the production of articles coming into contact with foodstuffs.

Another way of preparing phenol-urea-paraform resins was described by Crump and Lloyd<sup>44</sup> who melted the three constituents together without the aid of aqueous solution and completed the condensation by heating. The proportion of urea used is greater than that of the phenol, and the reaction mixture is kept neutral or

<sup>41</sup> H. L. Bender, U. S. P. 1,717,600, June 18, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 4090. British P. 280,520, 1926; *Chem. Abs.*, 1928, 22, 3508. French P. 643,438, 1927; *Chem. Abs.*, 1929, 23, 1617.

<sup>42</sup> A. Lloyd, U. S. P. 1,784,737, Dec. 9, 1930, to Bakelite, Ltd.; *Chem. Abs.*, 1931, 25, 389. British P. 302,612, 1927; *Chem. Abs.*, 1929, 23, 4308.

<sup>43</sup> H. L. Bender, U. S. P. 1,944,143, Jan. 16, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 2137.

<sup>44</sup> J. W. Crump and A. Lloyd, British P. 335,178, 1929, to Bakelite, Ltd.; *Chem. Abs.*, 1931, 25, 1400. French P. 697,267, 1930; *Chem. Abs.*, 1931, 25, 2867.

alkaline. The resins can be ground to a fine powder and are easily fusible, but become infusible on further heating. Goldschmidt and Neuss<sup>48</sup> heated urea and formaldehyde with an organic compound of acid character (phenol) that is capable of forming resinous products with formaldehyde. With small amounts of acid condensing media, clear or dull bodies were produced, according to the proportions of urea and aldehyde used. If larger amounts of acid media are employed, meerschäum-like substances are obtained. For example, 10 g. of phenol mixed with 94 g. of 30 per cent formaldehyde and 0.096 g. of concentrated sulphuric acid are refluxed, 20 g. of urea added and heating is continued until a thick, viscous mass results. After cooling and removing water by pressing, the material is hardened and dried, yielding a compact, waterproof, ivory-like product. The use of the acid condensing medium is said to effect a 15-17 per cent saving of formaldehyde. Neuss<sup>48</sup> also used resorcinol to replace phenol.

Resorcinol and analogous phenols were used by Howald<sup>49</sup> to modify urea-formaldehyde resins. The urea and formaldehyde are condensed in aqueous solution, water is removed and resorcinol is mixed with the dried condensation product. Quinol, orcinol, pyrogallol and phloroglucinol give similar results. The molded articles prepared with the use of resorcinol are not quite water-white, but they can be delicately tinted by incorporating dyes in the initial aqueous mixture.

Potter and Crump<sup>50</sup> developed a method for converting the intermediate products of the urea-phenol-formaldehyde condensation directly into the final hardened form by means of hardening agents. The first stage of the process consists in the combination of the 3 reactants by means of heat, followed by a dehydration which gives a syrupy resin.<sup>50</sup> The speed with which this resin will harden in a mold depends on the proportion of phenol to urea in the original syrup and on the nature and amount of the hardening agent. The hardening agents used include strong inorganic or organic acids and salts capable of conditioning an acid reaction (aniline hydrochloride, urea nitrate or ammonium chloride). The larger the ratio of urea to phenol, the more rapid is the hardening. By adding 10 per cent (calculated on the weight of the syrup) of urea nitrate to a syrup prepared from 100 parts of phenol, 34 parts of urea, 185 parts by volume of 40 per cent formaldehyde and 0.01 part by weight of oxalic acid, the first hardening phase is completed in 1 minute, and the resin becomes permanently hard and infusible in 1 hour.

Acid condensing agents have been utilized by a number of other investigators in the preparation of resins of this type. Nakamura<sup>51</sup> made a colorless and transparent resin by condensing phenol and formaldehyde in the presence of an acid catalyst and from 25 to 80 per cent of a urea-formaldehyde condensation product. The mixture can be dried and hardened at 80-130°C. A milk-white color is imparted to the resin by adding stearic or oleic acid or camphor oil. In making

<sup>48</sup> H. Goldschmidt and O. Neuss, U. S. P. 1,844,571, Feb. 9, 1932, to Synthetic Plastics Co., Inc.; *Chem. Abs.*, 1932, 26, 2073. U. S. P. 1,865,398, June 28, 1932; *Chem. Abs.*, 1932, 26, 4488. British P. 208,761, 1923; *Chem. Abs.*, 1924, 18, 1855. Austrian P. 95,663, 1924; Swiss P. 103,221; French P. 556,529; *Kunststoffe*, 1925, 15, 12. See also French P. 667,578, 1929, to Kunststoffsabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1930, 24, 1236.

<sup>49</sup> O. Neuss, British P. 202,651, 1923; *Chem. Abs.*, 1924, 18, 313. German P. 490,257, 1922, addn. to 484,972, to Kunststoffsabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1930, 24, 2558.

<sup>50</sup> A. M. Howald, U. S. P. 1,928,493, Sept. 26, 1933, to Toledo Synthetic Products, Inc.; *Chem. Abs.*, 1933, 27, 5996. British P. 373,184, 1932; *Chem. Abs.*, 1933, 27, 3837. Canadian P. 330,976, 1933; *Chem. Abs.*, 1933, 27, 3599. French P. 711,395 and 711,393, 1931; *Chem. Abs.*, 1932, 26, 1813.

<sup>51</sup> H. V. Potter and J. W. Crump, U. S. P. 1,667,675, Apr. 24, 1928, to Damard Lacquer Co., Ltd.; *Chem. Abs.*, 1928, 22, 2072. British P. 264,601, 1925; *Brit. Chem. Abs. B*, 1927, 228. W. F. Fleet and H. V. Potter, Canadian P. 265,519, 1926; *Chem. Abs.*, 1927, 21, 1031.

<sup>52</sup> W. F. Fleet and H. V. Potter, British P. 256,711, 1925, to Damard Lacquer Co., Ltd.; *Chem. Abs.*, 1927, 21, 3137. German P. 601,539, 1934, to Bakelite, Ltd.; *Chem. Abs.*, 1935, 29, 3748.

<sup>53</sup> M. Nakamura, U. S. P. 1,775,135, Sept. 9, 1930, to Sankyo K. K.; *Chem. Abs.*, 1930, 24, 5173.

similar resins, Crump<sup>51</sup> slowly added urea dissolved in part of the aldehyde to a solution of the phenol in the remainder of the formaldehyde, kept at the boiling point. Water and uncondensed reactants were removed from the initial condensation product (still in a soluble form) by distillation *in vacuo* in the presence of a neutral dehydrating agent capable of forming a constant-boiling mixture with water (e.g., butyl alcohol), followed by open-pan boiling. An alkaline condensing agent may be added toward the end of the condensation and an acid catalyst (oxalic acid) during the vacuum distillation. The ratio of phenol to urea may vary from 0.5:1 to 5:1, the lower ratios giving products for the manufacture of molded articles and the higher ones for the production of varnishes. Rothera, Blythen and Gillespie<sup>52</sup> described a resin prepared by warming urea or a urea derivative with an aldehyde for a short time, and then heating the primary reaction product with phenol or naphthol in an acid medium until solids in the form of resins are precipitated. Spitzer<sup>53</sup> precipitated plastic masses from colloidal solutions of resinous condensation products (from aldehydes and phenol or cresol) by the addition of urea-formaldehyde hydrosols. In another method, plastic substances are prepared by condensing urea with formaldehyde in the presence of phenol or a di- or polyphenol; rubber-like compositions being obtained on oxidation with a persulphate during or after condensation.<sup>54</sup> Cameron and Jackson<sup>55</sup> heated 1 mol of cresol at 100°C. with 2 mols of paraformaldehyde in the presence of triethanolamine, a dispersing agent (potassium bromide), urea and guanidine carbonate. The mixture is chilled rapidly to room temperature, and a liquid resin, that can be cured by heat, is formed. Melamid<sup>56</sup> submitted products obtained by condensing ketones and phenols with urea to a further condensation with aldehydes.

A colorless, transparent resin is formed by condensing phenol and formaldehyde in the presence of alkaline catalysts, acidifying and then adding a solution of urea in 40 per cent formaldehyde.<sup>57</sup> Thiourea is used to clarify the final product, and the initial condensation can be made with an acid catalyst. Ostersetzer and Riesenfeld<sup>58</sup> carried out an initial phenol-formaldehyde condensation in the presence of aqueous caustic potash and used phenols or urea in an acid medium as a binding agent for the uncombined aldehyde in the resinous product. Specifically, 1000 g. of phenol, 3000 g. of 30 per cent formaldehyde and about 50 cc. of 8 *N* potassium hydroxide are refluxed for a short time. Then, 18 cc. of 8 *N* lactic acid and about 58 cc. of a solution of phthalic anhydride in glycerol are added. The whole product is distilled *in vacuo*, 60 g. of urea being added during the distillation, and hardening being accomplished by heat treatment. Another species of synthetic resin is produced by fusing a non-hardening phenol-formaldehyde product, mixed with fillers, urea and paraformaldehyde.<sup>59</sup>

A phenolic gum (gum acceroides) may also be combined with urea and aldehydes, according to Novotny,<sup>60</sup> forming a thermosetting, resinous product. Fibrous materials (paper, cloth or wood flour) are incorporated in the mixture which is then sheeted and hardened. An addition of 10 per cent of dicyanodiamide (cal-

<sup>51</sup> J. W. Crump, U. S. P. 1,973,050, Sept. 11, 1934, to Bakelite, Ltd.; *Chem. Abs.*, 1934, 28, 7044. British P. 309,849, 1928; *Brit. Chem. Abs. B.*, 1929, 484.

<sup>52</sup> W. S. Rothera, S. Blythen and H. R. Gillespie, German P. 517,251, 1926; *Chem. Abs.*, 1931, 25, 2813. German P. 567,671, 1921, addn. to 563,037; *Chem. Abs.*, 1933, 27, 2541.

<sup>53</sup> A. Spitzer, Swiss P. 153,843, 1931; *Chem. Abs.*, 1933, 27, 1113.

<sup>54</sup> M. van Roggen and J. de Bielse, French P. 660,949, 1928; *Chem. Abs.*, 1930, 24, 212.

<sup>55</sup> H. J. Cameron and E. H. Jackson, British P. 364,304, 1930, to Brit. Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B.*, 1932, 272.

<sup>56</sup> M. Melamid, French P. 678,282, 1929; *Chem. Abs.*, 1930, 24, 3662.

<sup>57</sup> French P. 740,250 and 740,251, 1931, to Soc. Nobel Francaise; *Chem. Abs.*, 1933, 27, 2320.

<sup>58</sup> A. Ostersetzer and F. Riesenfeld, U. S. P. 1,892,848, Jan. 3, 1933, to Pollopas, Ltd.; *Chem. Abs.*, 1933, 27, 2359.

<sup>59</sup> British P. 818,883, 1929, to Bakelite G.m.b.H.; *Brit. Chem. Abs. B.*, 1930, 977.

<sup>60</sup> E. E. Novotny, U. S. P. 1,902,461, Mar. 21, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3351.

culated on the weight of the phenol) promotes the phenol-aldehyde reaction.<sup>41</sup> Phenol or its homologues will also form plastic masses when added to an aqueous solution of albumin in the presence of urea, ammonia and formaldehyde.<sup>42</sup> The mixture is congealed by heating or by acid substances, and hardening of the product is effected by the application of heat and pressure.

Phthalic anhydride was employed by Lougovoy<sup>43</sup> as a catalyst in forming phenol-urea-formaldehyde resins. A mixture composed of 120 parts of urea, 320 parts of 37-40 per cent formaldehyde, 94 parts of phenol and 20 parts of phthalic anhydride becomes milky on heating, and a resin, which cools to a hard, white mass insoluble in hot alcohol, acetone or benzene, separates. The resin is crushed, dried and molded at 120°C. under 2000 lb. pressure, giving products free from any reddish color. The milky solution formed in the early stages of the condensation can be diluted with an equal volume of alcohol and incorporated with fillers. The reaction can be carried out under anhydrous conditions, using paraform instead of aqueous formaldehyde. Hydrochloric or sulphuric acid can also be used in this process.<sup>44</sup> Using 100 parts of phenol, 25 parts of urea, 100 parts of aqueous formaldehyde and 2 parts of 50 per cent sulphuric acid and heating under reflux for 15 minutes, a slow-hardening resin is produced, that dissolves in hot acetone or in acetone-alcohol and benzene-methyl alcohol mixtures. The solutions dissolve nitrocellulose and are considered of value as coating compositions.

Spitzer<sup>45</sup> made thermohardening, light-resistant resins that dissolve in low-boiling solvents by causing formaldehyde to react with a phenol, urea and p-toluenesulphonamide.

Urea-formaldehyde-phenol condensation products were applied by Moss and Crutchfield<sup>46</sup> as an adhesive in the manufacture of laminated glass. The adhesive is prepared by refluxing 100 parts of phenol, 20 parts of urea and 150 parts of 40 per cent formaldehyde at 125°C. for 2 hours and vacuum distilling the resulting brown liquid until a soft resin remains. The product is soluble in alcohol, benzyl alcohol, ethyl lactate and acetone. Coating compositions composed of 10 parts of this resin, 4 parts of diethyl phthalate, 30 parts of acetone and 10 parts of alcohol are used to hold a celluloid sheet between layers of glass. Glass sheets are joined to a cellulose derivative by means of a phenol-urea reaction product in conjunction with other adhesives, including Canada balsam or euphorbium resin.<sup>47</sup>

Becherer<sup>48</sup> prepared a water-soluble product by treating a phenol-urea-formaldehyde resin with additional phenol and then at a raised temperature with a sulphonating agent. As an example, 80 parts of a resin (made by condensing 100 parts of phenol with 20 parts of urea and 120 parts of a 38 per cent formaldehyde solution at 85°C. in the presence of 2.5 parts of 40 per cent sulphuric acid) are stirred with 100 parts of phenol at 70° C. until a homogeneous solution is produced. Then, at a temperature of 40-110°C., 100 parts of sulphuric acid (sp. gr. 1.8354) are introduced and stirring is continued until a sample of the product is soluble in its own volume of water. After neutralizing the excess acid with sodium carbonate, the soluble resin can be salted out or separated by evaporation. These resins can be employed, according to Becherer, as tanning agents, mordants and wool reserving agents in the leather and textile industries.

<sup>41</sup> E. C. Rossiter and W. C. Davis, U. S. P. 1,857,478, May 10, 1932; *Chem. Abs.*, 1932, 26, 3945.

<sup>42</sup> German P. 573,516, 1933, to Jaroslaw's Erste Glimmerwarenfabr.; *Chem. Abs.*, 1933, 27, 4363.

<sup>43</sup> B. N. Lougovoy, U. S. P. 1,756,252, Apr. 29, 1930, to Ellie-Foster Co.; *Chem. Abs.*, 1930, 24, 3122.

<sup>44</sup> B. N. Lougovoy, U. S. P. 1,779,551, Oct. 28, 1930; *Chem. Abs.*, 1931, 25, 224.

<sup>45</sup> A. Spitzer, British P. 409,490, 1933; *Brit. Chem. Abs. B*, 1934, 591. French P. 752,231, 1933; *Chem. Abs.*, 1934, 28, 920.

<sup>46</sup> W. H. Moss and K. H. Crutchfield, U. S. P. 1,870,018, Aug. 2, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 5396. Canadian P. 323,574, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 4432. British P. 342,337 and 342,458, 1929, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B*, 1931, 395.

<sup>47</sup> C. H. Field and D. Haslett, British P. 321,173, 1928; *Chem. Abs.*, 1930, 24, 2567.

<sup>48</sup> F. Becherer, U. S. P. 1,982,619, Dec. 4, 1934, to J. R. Geigy S. A.; *Chem. Abs.*, 1935, 29, 525. German P. 596,716, 1934; *Chem. Abs.*, 1934, 28, 5263.

Sulphonated phenols combined with thiourea-aldehyde or urea-aldehyde products were used in tanning by Somerville and Raterink.<sup>66</sup> These investigators found that urea derivatives act as retarding agents in the interaction of sulphonated phenols and aldehydes, thus controlling the reaction. The color of the condensed sulphonic acid is improved, and the synthetic tanning materials developed give white leather. The sulphonation of the phenol is performed by heating 94 lb. of phenol to 40°C., slowly adding 153 lb. of sulphuric acid (sp. gr. 1.8354) and heating at 95-100°C. for 2 hours. The solution is cooled, 70 lb. of water are added at 35°C., 15 lb. of thiourea stirred in during a period of 10 minutes, 63 lb. of 38 per cent formaldehyde added rapidly, and the temperature is then raised to



FIG. 114.—  
Introduction of Dyes, etc.,  
into Top of Polymerizing  
Kettle.

*Courtesy Catalin Corp.*

80-85°C. for an hour. After cooling the solution, the free acid is neutralized with sodium hydroxide, and water is added until the weight is increased to 470 lb. The solution can then be employed in the tanning process. Tanning materials were prepared also by the condensation of sulphonated derivatives of phenols, cresols and naphthols with the reaction products from urea, formaldehyde and ammonium sulphide or ammonium thiocyanate.<sup>70</sup> The resulting acid products are partially neutralized by oxides or hydrates of heavy metals. According to Pollak,<sup>71</sup> formaldehyde or acetaldehyde may be condensed with a polyvalent phenol (resorcinol) together with urea and vegetable tanning materials at a temperature below 50°C. in the presence of an acid condensing agent. The final products are water-soluble tanning compounds. Condensation products of urea and formal-

<sup>66</sup> I. C. Somerville and H. R. Raterink, U. S. P. 1,919,756, July 25, 1933, to Röhm and Haas Co; *Chem. Abs.*, 1933, 27, 4952. U. S. P. 1,951,564, Mar. 20, 1934; *Brit. Chem. Abs. B*, 1935, 163. British P. 388,969, 1933; *Chem. Abs.*, 1933, 27, 4715.

<sup>70</sup> French P. 723,318 and 720,712, 1930, to Progil (Soc. anon.) *Chem. Abs.*, 1932, 26, 4204. German P. 562,826, 1930; *Chem. Abs.*, 1933, 27, 1231. British P. 388,475, 1931; *Brit. Chem. Abs. B*, 1933, 400. British P. 383,381, 1931; *Brit. Chem. Abs. B*, 1933, 117.

<sup>71</sup> L. Pollak, British P. 353,872, 1930; *Brit. Chem. Abs. B*, 1931, 1149.

dehyde added to a sulphonated phenol give alkali-soluble compositions used as tanning substances and also for weighting silk.<sup>72</sup>

Other investigators developed methods of alkaline condensation of urea and formaldehyde in the presence of substances (phenols, aniline and naphthylamine) capable of resin-formation with the aldehyde.<sup>73</sup> Kraus<sup>74</sup> formed a urea-formaldehyde resin in the presence of hexamethylenetetramine. This worker also suggested that a hexamethylenetetramine-phenol condensate be incorporated with a urea-formaldehyde resin. Starch, glue or gum arabic may be added to further modify the product.<sup>75</sup>

Salicylic acid was studied in connection with urea-aldehyde resins by Belfit.<sup>76</sup> The urea-formaldehyde resin is formed as an unhardened, liquid product, and to 81 cc. of this condensate are added 5 g. of salicylic acid, using 50 cc. of ethyl lactate as a solvent. The resulting lacquer necessarily contains some water, but the aqueous content should be kept as low as possible. Films from this coating composition (after hardening by a heat-treatment at 130-150°C.) are reported to be resistant to solvents and chemical reagents. If a small amount of castor oil is added to the lacquer, the resulting films are more pliable. Salicylic acid may be replaced by ammonium salicylate, acetylsalicylic acid, hydroxynaphthoic acids, gallic acids, metal salicylates or salicylamide. Arnot<sup>77</sup> also used salicylic acid, gallic acid and cresols for modifying urea resins. As early as 1904, Voswinkel and Lauch<sup>78</sup> produced for use in pharmacy a series of condensation products from tannin or its derivatives, urea and formaldehyde. Goldsmith<sup>79</sup> described a thermoplastic product that he obtained by subjecting gluten to the combined action of formaldehyde and  $\beta$ -naphthol. Voswinkel<sup>80</sup> used gallic acid for condensation with urea and formaldehyde, hydrochloric acid being the condensing agent.

#### MOLDING COMPOSITIONS WITH CASEIN

As early as 1910, Goldsmith<sup>81</sup> prepared a casein or gluten composition containing urea and formaldehyde. The function of the urea, however, was to serve as a softening or fluxing agent, unlike the present-day use of urea in urea-formaldehyde molding compositions. In this early work, urea was added (as one of a number of alternatives) to proteins (casein or gluten) and formaldehyde, forming a thermoplastic composition.

The incorporation of protein bodies such as casein, gelatine or glue with urea-formaldehyde resins is found to improve the molding properties of the resin, and was applied to this purpose by a number of workers. Redman<sup>82</sup> mixed 100 parts of casein, 100 parts of urea, 100 parts of paraformaldehyde, 50 parts of water, 40 parts of ethylene glycol and 13 parts of aqueous ammonia in a ball mill. The resin-forming reaction takes place on sheeting rolls to which the mixture is transferred, and the volatile components, including the reaction-water, are largely driven

<sup>72</sup> British P. 305,013, 1928, to J. R. Geigy A.-G.; *Chem. Abs.*, 1929, 23, 4844.

<sup>73</sup> British P. 302,737, 1927, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1929, 23, 4357. Swiss P. 143,726, 1929; *Chem. Abs.*, 1931, 25, 4739. French P. 665,899, 1928; *Chem. Abs.*, 1930, 24, 1530.

<sup>74</sup> W. Kraus, French P. 773,955, 1934; *Chem. Abs.*, 1935, 29, 2261.

<sup>75</sup> W. Kraus, French P. 773,919, 1934; *Chem. Abs.*, 1935, 29, 2261. French P. 777,663, 1935; *Chem. Abs.*, 1935, 29, 4103.

<sup>76</sup> R. W. Belfit, U. S. P. 1,898,709, Feb. 21, 1933, to Scovill Mfg. Co.; *Chem. Abs.*, 1933, 27, 2831.

<sup>77</sup> R. Arnot, British P. 290,327, 1927; *Brit. Chem. Abs. B*, 1928, 532. French P. 648,906, 1928; *Chem. Abs.*, 1929, 23, 3115.

<sup>78</sup> A. Voswinkel and R. Lauch, U. S. P. 828,908, Aug. 21, 1906; *Chem. Abs.*, 1907, 1, 124. British P. 23,569, 1904; *J.S.C.I.*, 1905, 24, 103.

<sup>79</sup> B. B. Goldsmith, U. S. P. 964,964 and 965,137, July 19, 1910; *Chem. Abs.*, 1910, 4, 2744.

<sup>80</sup> A. Voswinkel, German P. 171,783, 1906; *Chem. Zentr.*, 1906, 2, 469.

<sup>81</sup> B. B. Goldsmith, U. S. P. 965,137, July 19, 1910; *Chem. Abs.*, 1910, 4, 2745. U. S. P. 964,964, July 19, 1910; *Chem. Abs.*, 1910, 4, 2744.

<sup>82</sup> L. V. Redman, U. S. P. 1,732,533, Oct. 22, 1929, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 258. British P. 329,628, 1929; *Chem. Abs.*, 1930, 24, 6042.

off at this point. The almost anhydrous mixture obtained possesses good molding characteristics under standard conditions, yielding infusible articles little affected by neutral solvents. The surface appearance and water resistance of the molded products are enhanced by the addition of cellulose esters, and plasticizers (diethyl or dibutyl oxalates, tartrates or phthalates) improve the working qualities.

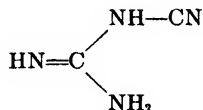
Landecker<sup>55</sup> found that a mixture of dry, powdered casein and urea added to water formed a glue, joints made with this composition being hardened by the inclusion of formaldehyde in the casein-urea solution. On adding excess of water to the casein-urea solution, an albuminous precipitate is formed. When this is filtered off, dried and molded with heat and pressure, a transparent, artificial horn is obtained. The molding pressure is materially lower than that required to mold casein alone. According to Ott, Schussler, Luther and Henek,<sup>56</sup> a mixture of 500 parts of casein and 500 parts of dimethylolurea, on being subjected to a pressure of 200 atmospheres for 3.5 hours at 100°C., gives a yellowish resinous mass. The casein is regarded by Schmidt<sup>55</sup> as a "carrier substance" in such a mixture. Thus, urea or its derivatives is condensed with formaldehyde and then dehydrated at 40-45°C. in the presence of carriers (casein, cellulose or its derivatives and certain natural or synthetic resins) in a kneading machine or between rollers. The final hot molding is similar to that used in processes already described.

A plasticizer obtained by condensing thiourea and formaldehyde was used by Bussard<sup>56</sup> to increase the fluidity of condensation products from ureides and formaldehyde.

#### RESINS FROM CYANAMIDE AND ALLIED SUBSTANCES

Cyanamide yields resins under conditions similar to those employed in the production of urea resins, and these resins show approximately similar properties. In acid solution, cyanamide hydrolyzes to urea,<sup>57</sup> and in the following an acid medium is sometimes employed.

Dicyanodiamide, which is capable of functioning as the urea derivative cyanoguanidine



was condensed by Wallasch<sup>58</sup> with formaldehyde in the presence of mineral acids, giving a viscous resin said to be of use as an adhesive.

Tomita<sup>59</sup> found that gelatinous products resulted on prolonged heating of a mixture of 300 cc. of a 3 per cent dicyanodiamide solution and 10 cc. of a 40 per cent formaldehyde solution. By acidifying the mixture with acetic acid or nitric acid, however, the gelatinous substance is formed at ordinary temperatures, but no such compound results when any other acid is used. After drying in air

<sup>55</sup> M. Landecker, U. S. P. 1,725,805, Aug. 27, 1929, to American Nuplex Corp.; *Chem. Abs.*, 1929, 23, 5018.

<sup>56</sup> K. Ott, H. Schussler, M. Luther and C. Henek, Canadian P. 284,967, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 942. British P. 268,804, 1926; *Chem. Abs.*, 1928, 22, 1447.

<sup>57</sup> F. Schmidt, British P. 281,993, 1927; *Chem. Abs.*, 1928, 22, 3746. French P. 686,219, 1927; *Chem. Abs.*, 1929, 23, 247. German P. 591,045, 1934; *Chem. Abs.*, 1934, 28, 2556. German P. 597,349, 1934; *Chem. Abs.*, 1934, 28, 5264.

<sup>58</sup> C. Bussard, French P. 667,832, 1929; *Chem. Abs.*, 1930, 24, 1476.

<sup>59</sup> J. H. Lidholm, Swedish P. 54,246, 1923, to Aktiebolaget Wargoen. *Chem. Abs.*, 1923, 17, 3345. See also E. Johnson, Norwegian P. 44,060, 1927; *Chem. Abs.*, 1928, 22, 4214.

<sup>58</sup> H. Wallasch, German P. 323,665, 1915; *J.S.C.I.*, 1920, 39, 759A. German P. 325,647, 1919; *J.S.C.I.*, 1921, 40, 55A.

<sup>59</sup> E. Tomita, *J. Chem. Ind. Japan*, 1924, 27, 774; *Chem. Abs.*, 1925, 19, 562.

at 25-30°C., the product becomes an elastic, glassy material, softening at 40°C., and it is used as an adhesive for wood, glass and porcelain.

Ripper<sup>90</sup> dissolved 100 parts of dicyanodiamide with 71 parts of urea in 200 parts by weight of a 40 per cent aqueous formaldehyde solution and refluxed the mixture for 2 hours. The water-clear reaction mixture is poured into water, and the resin separates as a flour-like powder which may be molded, after washing and drying, to give transparent articles. No catalysts or condensing agents are employed in this reaction. The condensation products of dicyanodiamide and formaldehyde with casein also furnish molding powders.<sup>91</sup> The casein is added during the condensation of the other reactants. In place of dicyanodiamide, urea or thiourea may be used. A dry mixture of dicyanodiamide, an albuminous material and a polymer of formaldehyde may be molded under heat and pressure.

The condensation of dicyanodiamide and formaldehyde may be carried out at a controlled  $p_H$  of 8-10 in the presence of a buffering mixture and sodium hydroxide, with an addition of metal salts (copper sulphate or zinc chloride).<sup>92</sup> This process yields a hydrophobic, heat-convertible resin. As an example of the manufacture of a resin of this type containing phenol,<sup>93</sup> 100 parts of dicyanodiamide and 112 parts of phenol are refluxed with 200 parts of formaldehyde for 2.5 hours, and the mixture is poured into cold water. The solid resin obtained is powdered, washed and dried, forming a molding powder with excellent flow characteristics. The products molded from this powder are slightly yellowish and transparent.

Variation in the proportion of formaldehyde used in the dicyanodiamide resins gives a wide modification of their properties.<sup>94</sup> Thus, 1 mol of dicyanodiamide condensed with 2 mols of formaldehyde for 3 hours at 60-80°C. yields a clear solution, from which a transparent resin, that can be mixed with urea or thiourea condensation products, is formed on evaporation. A molding powder, which flows easily and gives products that readily part from the mold, is prepared from 10 parts of dicyanodiamide and 10.7 parts of formaldehyde. Urea and thiourea serve as additional constituents in a large number of these resins. The interaction of 30 parts of dicyanodiamide, 58 parts of formalin and 12.6 parts of formic acid, after some hours heating, produces a transparent jelly, soluble in water. On heating the jelly for several hours at 80-90°C., a clear, brittle resin is obtained which swells like gelatin (with which it is miscible) in water and then dissolves. As the amount of formic acid employed decreases, the water-solubility of the product also lessens. A highly adhesive resin solution is obtained by mixing 84 parts of a urea-thiourea-formaldehyde condensation product, 16 parts of dicyanodiamide-formaldehyde resin and 1.3 parts of formic acid. The solution is evaporated on a water-bath until it contains about 20 per cent of water.

Sulphuric and hydrochloric acids give similar but less soluble jellies. The condensation of dicyanodiamide and formaldehyde in the presence of linoleic acid or stearic acid leads to the formation of soft, pale yellow resins that harden on exposure to air and can be used in the manufacture of varnishes. Ricinoleic acid also gives a clear soft resin, insoluble in water and benzene, but soluble in alcohol, hot ethylene glycol or a mixture of cyclohexanol and benzene. The resin is formed in these cases by heating the constituents together and then evaporating. The condensation products formed by using oleic, linoleic and ricinoleic acids are miscible with rubber and their use as plasticizers has been proposed. With oxalic acid, hard, white, brittle resins are obtained. Dicyanodiamide, in a quantity not exceeding 10 per cent of the amount of phenol, is used as a condensing agent in

<sup>90</sup> K. Ripper, U. S. P. 1,951,772, Mar. 20, 1934; *Chem. Abs.*, 1934, 28, 3540. German P. 548,871, 1928; *Chem. Abs.*, 1932, 26, 4190. British P. 287,177, 1927; *Chem. Abs.*, 1929, 23, 533.

<sup>91</sup> K. Ripper, U. S. P. 1,952,941, Mar. 27, 1934; *Chem. Abs.*, 1934, 28, 3849. British P. 297,423 and 323,047, 1928; *Brit. Chem. Abs. B*, 1930, 204. German P. 559,105, 1928; *Chem. Abs.*, 1930, 27, 817.

<sup>92</sup> K. Ripper, British P. 382,271, 1932, addn. to 287,177; *Chem. Abs.*, 1933, 27, 4481. French P. 719,711, 1931; *Chem. Abs.*, 1932, 26, 3946. German P. 530,732, 1930; *Chem. Abs.*, 1932, 26, 267.

<sup>93</sup> K. Ripper, U. S. P. 1,812,374, June 30, 1931; *Chem. Abs.*, 1931, 25, 4983.

<sup>94</sup> E. C. Rossiter, British P. 314,358, 1927, to Brit. Cyanides Co., Ltd.; *Chem. Abs.*, 1930, 24, 1529.

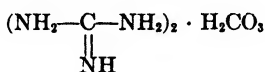


making synthetic resins from phenols and aldehydes.<sup>96</sup> A formaldehyde-dicyanodiamide resin (30 parts) mixed with 70 parts of gelatin in aqueous solution can be used as an adhesive for glass sheets.<sup>96</sup> Schmidt<sup>97</sup> condensed formaldehyde and cyanamide in an aqueous solution containing a strong, inorganic acid by heating the mixture on a water-bath until the products separated in an amorphous condition. The condensation also may be carried out in a dilute, alkaline solution. A cyanamide solution prepared by treating crude calcium cyanamide with water may be used. John<sup>98</sup> described the condensation with formaldehyde of a filtered solution obtained by leaching, at 30-50°C., calcium cyanamide with water containing carbon dioxide. The leached solution contains cyanamide, dicyanodiamide, urea, calcium carbamate and guanidine. It is concentrated slightly by evaporation and then condensed in the presence of a little hydrochloric acid with formaldehyde, forming a gelatinous and finally horny mass. Calcium salts are removed, before or after condensation, by the addition of very dilute sulphuric or oxalic acid.

Thiodicyanodiamidine, already formed or prepared *in situ* by reacting cyanamide or dicyanodiamide with hydrogen sulphide, may be condensed with formaldehyde in alkaline solution.<sup>99</sup> The product is neutralized or acidified and heated, and a urea-formaldehyde condensation product may be added. After evaporating *in vacuo* to a thick syrup, the resin is mixed with fillers and molded. Rothera, Blythen and Gillespie<sup>100</sup> also prepared resins by the alkaline condensation of formaldehyde and thiodicyanodiamidine.

#### USE OF GUANIDINE

Guanidine, prepared from ammonium thiocyanate, forms resins with formaldehyde in the same way as urea.<sup>101</sup> Guanidine thiocyanate and guanidine carbonate give crystalline or amorphous resins that may be pressed. Guanidine derivatives and thiourea also give molding products with formaldehyde. The presence of water makes the resin opaque and liable to crack, but this difficulty is minimized by an addition of glycerol. Stine<sup>102</sup> described the preparation of synthetic resins from guanidine salts or derivatives and aqueous formaldehyde. The formula of guanidine carbonate, typical of the salts employed, is:



Benzaldehyde, acetaldehyde and other aldehydes may be employed instead of formaldehyde. As an example, 40 parts of 40 per cent formalin are refluxed with 15 parts of guanidine carbonate for 20 minutes. The resulting solution sets to a gel that forms a transparent resin on heating for 24 hours in a vacuum oven at 50°C. Further heating at 100°C. makes the product hard and infusible.

Guanidine was used in urea-formaldehyde condensations by Griffith.<sup>103</sup>

<sup>96</sup> E. C. Rossiter and W. C. Davis, British P. 327,154, 1928, to Brit. Cyanides Co., Ltd.; *Chem. Abs.*, 1930, 24, 5173. French P. 665,210, 1928; *Chem. Abs.*, 1930, 24, 982.

<sup>97</sup> E. C. Rossiter, British P. 344,047, 1929, to Brit. Cyanides Co., Ltd.; *Chem. Abs.*, 1932, 26, 3344.

<sup>98</sup> H. Schmidt, U. S. P. 1,791,433 and 1,791,434, Feb. 3, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1645. British P. 319,322, 1928; *Chem. Abs.*, 1930, 24, 2559. German P. 530,830, 1933, addn. to 522,056; *Chem. Abs.*, 1934, 28, 261.

<sup>99</sup> H. John, German P. 394,493, 1919; *J.S.C.I.*, 1924, 43, 840B.

<sup>100</sup> British P. 347,228, 1929, to Kunststoffsabr. F. Pollak G.m.b.H.; *Chem. Abs.*, 1932, 26, 2880. French P. 689,409 and 689,410, 1930; *Chem. Abs.*, 1931, 25, 5050.

<sup>101</sup> W. S. Rothera, S. Blythen and H. R. Gillespie, German P. 532,381, 1930; *Chem. Abs.*, 1932, 26, 569. See also W. Kraus, U. S. P. 2,002,540, May 28, 1935, to American Cyanamid Co.; *Chem. Abs.*, 1935, 29, 4479.

<sup>102</sup> K. Keller and W. Nüssler, *Ber. Ges. Kohlentech.*, 1931, 4, 34; *Chem. Abs.*, 1932, 26, 1808.

<sup>103</sup> C. M. Stine, U. S. P. 1,780,636, Nov. 4, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 224.

<sup>104</sup> P. W. Griffith, U. S. P. 1,653,597, Feb. 7, 1928, to American Cyanamid Co.; *Chem. Abs.*, 1928, 22, 1344.

Guanidine salts make it possible to obtain colorless urea-formaldehyde resins over a wide pH range. In the method, the guanidine carbonate-urea mixture is refluxed with 2 mols of formaldehyde solution, evaporated and then dried, yielding a colorless, transparent resin.

A colorless, vitreous material is made by condensing urea and guanidine with formaldehyde in the presence of powdered zinc, trioxymethylene and hexamethylenetetramine. After boiling 1-3 hours the mass is filtered, freed from water at 25-40°C. and may be preserved as fluid or solidified.<sup>104</sup>

#### RESINS FROM ALDEHYDES AND URETHANS

The condensation of aqueous formaldehyde with urethan in the presence of hydrochloric acid forms methyleneurethan ( $\text{CH}_2=\text{N}-\text{COOC}_2\text{H}_5$ ) which gives trimeric methyleneurethan when boiled with dilute acetic acid.<sup>105</sup> If the oily reaction product is heated with acetic acid until all of the latter has been removed, resinous tetrameric methyleneurethan remains. A urethan such as methylol butyl urethan (2-5 per cent) is added to drying oil paints in order to obtain smooth, glossy finishes with white pigments (zinc oxide).<sup>106</sup> Water-insoluble urea derivatives or urethans with equal amounts of cellulose derivatives are used in the production of patterned films, sheets and coatings.<sup>107</sup> N-Methylolurethans are prepared by treating urethan with a polymer of formaldehyde in the presence of an alkaline condensing agent.<sup>108</sup> The methylol derivatives of urethan are stable at ordinary temperatures but yield formaldehyde when heated. A mixture of casein, methylol butyl urethan, water, butanol and acetone gives an interesting molded product when hot-pressed.<sup>109</sup> A mixture of urethan and urea will also condense with formaldehyde in an acid medium.<sup>110</sup> With an acid contact agent and at high temperatures, urea and urethan condense with aqueous formaldehyde to form products that may be hardened.<sup>111</sup>

#### MISCELLANEOUS MODIFICATIONS

Sulphur derivatives (thioaldehydes) of formaldehyde or benzaldehyde give soluble condensation products with urea.<sup>112</sup> The actual process entails pouring ammonium sulphide solution into urea (which dissolves) and adding formaldehyde solution. The liquid mixture sets to a crystalline mass on standing for 2-4 days in contact with aluminum. The products can be made insoluble (in water) by evaporation or by treatment with acids or alkalies. Conversely, the insoluble material yields substances dissolving in alcohol or water when treated with ammonium thiocyanate and additional formaldehyde. De Granville and Davion<sup>113</sup> added a sulphide

<sup>104</sup> L. Segond, French P. 769,043, 1934, to Soc. anon. international Holding Radial; *Chem. Abs.*, 1935, 29, 534.

<sup>105</sup> M. Giua and G. Racciu, *Atti accad. sci. Torino*, 1929, 54, 300; *Chem. Abs.*, 1930, 24, 3212. The photosensitiveness of urethans was studied by A. Kórczynski and S. Grzybowski, *Gazz. chim. ital.*, 1923, 53, 94; *Chem. Abs.*, 1923, 17, 2277.

<sup>106</sup> K. Ott and H. Bernard, U. S. P. 1,897,528, Feb. 14, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2829.

<sup>107</sup> British P. 358,761, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 31.

<sup>108</sup> British P. 309,108, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 352.

<sup>109</sup> K. Ott and H. Schlüssel, German P. 575,927, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4890.

<sup>110</sup> French P. 724,943, 1931, to Bakelite G.m.b.H.; *Chem. Abs.*, 1932, 26, 4925.

<sup>111</sup> W. Kraus, German P. 589,969, 1933; *Chem. Abs.*, 1934, 28, 2450.

<sup>112</sup> British P. 313,455, 1923, to Pfenning-Schumacher-Werke G.m.b.H.; *Chem. Abs.*, 1930, 24, 1189. French P. 673,642, 1929; *Chem. Abs.*, 1930, 24, 3615. French P. 39,384, 1930, addn. to 673,642; *Chem. Abs.*, 1932, 26, 2287. British P. 366,009 and 366,065, 1930, addns. to 313,455; *Brit. Chem. Abs. B.*, 1932, 260. German P. 589,236, 1933; *Chem. Abs.*, 1934, 28, 1484. German P. 587,643, 1933; *Chem. Abs.*, 1934, 28, 1822. German P. 588,870, 1933, addn. to 587,643; *Chem. Abs.*, 1934, 28, 2137. See also French P. 767,899, 1934, to Du Pont Viscoid Co.; *Chem. Abs.*, 1935, 29, 524.

<sup>113</sup> J. de Granville and L. Davion, French P. 761,177 and 761,178, 1934; *Chem. Abs.*, 1934, 28, 4256.

during the condensation of urea and an excess of formaldehyde, in a medium brought to a  $p_H$  of 7 by means of potassium bitartrate, to assist fixation of sulphur on the resulting products. Colloidal sulphur, also, may be added to a condensation mixture with a  $p_H$  of 5. The mixture is then heated at 60°C. for 20 minutes and cooled quickly to 15°C. The resin is dried at 85°C. and ground, during which process p-toluenesulphamide and aluminum stearate are added. Armenault<sup>114</sup> produced plastic materials containing combined sulphur by treating urea-formaldehyde solutions with nascent hydrogen sulphide (formed *in situ* by the addition of a sulphide or polysulphide and an acid). Resins stated to possess elasticity and water-resistance can be prepared by condensing urea and formaldehyde in the presence of a compound containing the group -SS- (e.g., an alkali polysulphide or xanthate).<sup>115</sup>

Landecker<sup>116</sup> prepared a resin by dissolving 100 g. of urea in a solution containing 20 g. of ammonium sulphide and 250 cc. of commercial 40 per cent formaldehyde. The cloudiness of the solution disappears on warming, and a reaction which converts the liquid to a syrup and finally to a jelly takes place on boiling. The final product is a clear, highly refractive, solid mass which hardens on slow heating. A milky jelly, which can be molded into ivory-like articles, is obtained if sodium thiosulphate and formic acid are added to the urea-formaldehyde solution. The general properties of these resins somewhat resemble those of the natural albumins.

The problem of preserving urea-formaldehyde resins from deterioration due to liberation of formic acid was investigated by Lauter<sup>117</sup> who added an aromatic sulphonamide to the product. This type of compound is capable of taking up formic acid as it is formed. Thus, 706 g. of a 50 per cent, alcoholic solution of formaldehyde and 171 g. of p-toluenesulphonamide are heated to boiling, 180 g. of urea are added, and the mixture is refluxed until condensation is completed. The liquid product is mixed with fillers and molded.

Plastic products are obtained by condensing urea with formaldehyde and adding starch or flour in an amount equal to several times the weight of urea.<sup>118</sup> The addition can be made at any time during the operation. The products are hardened under pressure at 120-150°C. and are used for making buttons and similar articles. Natural or synthetic resins may be used as additional constituents and serve to increase the water-resistance. Organic colloids (e.g., agar-agar, proteins) may be present during the urea-formaldehyde condensation.<sup>119</sup> Gum tragacanth or starch were reported by Lionne<sup>120</sup> to retard the further condensation of urea-formaldehyde resins that were in the jelly stage. Proteins (e.g., casein) were added by Poulverel<sup>121</sup> during the resin-forming condensation of urea, phenol and formaldehyde in the preparation of plastic masses.

Seebach<sup>122</sup> prepared a hardenable product by treating urea with acetamide and

<sup>114</sup> R. Armenault, French P. 752,705, 1933, to Fabr. de prod. de chim. org. de Laire; *Chem. Abs.*, 1934, 28, 1154.

<sup>115</sup> I. Kreidl, British P. 416,661, 1932; *Brit. Chem. Abs. B.*, 1934, 1022. Austrian P. 136,993, 1934; *Chem. Abs.*, 1934, 28, 4616. French P. 765,269, 1934, *Chem. Abs.*, 1934, 28, 7044. The process may be modified by using compounds containing oxygen as well as the group -SS-. See I. Kreidl, Austrian P. 139,451, 1934, addn. to 136,993; *Chem. Abs.*, 1935, 29, 1537.

<sup>116</sup> M. Landecker, U. S. P. 1,904,244, Apr. 18, 1933; *Chem. Abs.*, 1933, 27, 3300.

<sup>117</sup> F. Lauter, U. S. P. 1,672,848, June 5, 1928, to Rohm & Haas Co.; *Chem. Abs.*, 1928, 22, 2673.

<sup>118</sup> German P. 569,342, 1927, to "Silur" tech. und chem. Produkte G.m.b.H.; *Chem. Abs.*, 1933, 27, 2260. British P. 287,727, 1927; *Brit. Chem. Abs. B.*, 1928, 419.

<sup>119</sup> J. de Granville and L. Davion, French P. 769,275, 1934; *Chem. Abs.*, 1935, 29, 525.

<sup>120</sup> E. Lionne, U. S. P. 1,901,373, Mar. 14, 1933; *Chem. Abs.*, 1933, 27, 3095.

<sup>121</sup> A. Poulverel, French P. 662,227, 1928; *Chem. Abs.*, 1930, 24, 476. It is reported that a resin from soya bean protein, urea, phenol, formaldehyde, cellulose and carbohydrates has found use in molded parts for automobiles. See *Chem. Met. Eng.*, 1935, 42, 313.

<sup>122</sup> F. Seebach, German P. 579,748, 1933, to Bakelite G.m.b.H.; *Chem. Abs.*, 1934, 28, 1153. German P. 595,462, 1934; *Chem. Abs.*, 1934, 28, 5694. Canadian P. 349,393, 1935, to Bakelite G.m.b.H., to Bakelite Corp.; *Chem. Abs.*, 1935, 29, 4104.

formaldehyde. The resin is dried, powdered, incorporated with filling materials and plasticizers and molded, being hardened by hot pressing. By kneading initial condensation products of the urea-formaldehyde type with substances capable of swelling (e.g., casein, cellulose or starch), Schmidt<sup>128</sup> obtained a dry composition that could be molded directly.

Printing color compositions were prepared by Paquin<sup>124</sup> by treating urea with aliphatic aldehyde-ammonia at 60-150°C. These compositions produce prints with enhanced depth of color when used with vat dyes such as those of the anthraquinone series. A resin can be obtained by condensing urea with formaldehyde in the presence of aryl ethers of glycols, according to Frick.<sup>126</sup> About 0.5 mol of the glycol derivative is used for each mol of urea. Water-soluble resins having emulsifying and wetting properties are prepared by heating aldols with urea at 110-120°C.<sup>125</sup> This product can be used to prepare wood and other surfaces for coating with cellulose lacquers.<sup>127</sup> Emulsifying agents are also obtained by condensing amino-alcohols with synthetic resin acids made by reacting natural resins with phenol-aldehyde and urea-aldehyde condensation products.<sup>128</sup>

By adding urea to fused chlorinated rubber and treating the mixture with formaldehyde in the presence of colophony or resin oils, Plauson<sup>129</sup> prepared water-resistant resins intended to be used as insulating materials. Alternatively, the urea may be added to fused chlorinated rubber, the mixture emulsified in water, and then treated with aqueous formaldehyde to give an emulsion.

The reaction between urea or its derivatives and solid polymerized formaldehyde can be effected in a melt of a solid hydrocarbon or a solid nitrated, chlorinated or hydrogenated substance.<sup>130</sup> Urea-formaldehyde condensation products give special resin compositions when mixed with casein, proteins, plastifying agents and glycol.<sup>131</sup> A product which forms elastic films and that can be used in aqueous solution as a coating for wood, textiles or metal is made by adding  $\beta$ -hydroxy-trimethylene sulphide to a urea-formaldehyde condensation product, during or after reaction.<sup>132</sup>

Spindler<sup>133</sup> prepared an organic glass by reacting carbon monoxide with ammonia at high pressures and at a temperature of 150-400°C. in the presence of a catalyst (iron, nickel, cobalt, copper or their compounds), forming urea and formaldehyde that combined in the usual manner. A thermohardening, colorless resin is prepared, according to Walter,<sup>134</sup> by condensing formaldehyde with p-sulphamino-benzamide (a by-product of saccharin manufacture).

Levi<sup>135</sup> found that ammonium N-disubstituted dithiocarbamates (NRR'-CS—NH<sub>2</sub>) react with glyoxal to yield solids that resinify more or less rapidly. Roll and Adams<sup>136</sup> described resins obtained from diphenyl carbodiimide. Auwers and Frese<sup>137</sup> reported that amorphous products with high melting points were formed by condensing 5-methyl-7-aminoindazol with urea. A number of resins occur also among the methylenediamide derivatives prepared by Bögemann and

<sup>128</sup> F. Schmidt, German P. 591,045, 1934; *Chem. Abs.*, 1934, 28, 2556.

<sup>124</sup> M. Paquin, U. S. P. 1,909,221, May 16, 1933, to General Aniline Works; *Chem. Abs.*, 1933, 27, 3832.

<sup>126</sup> F. Frick, German P. 517,430, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2313.

<sup>125</sup> German P. 509,163, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 835.

<sup>127</sup> British P. 281,310, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 3543.

<sup>128</sup> H. Dreyfus, British P. 394,657, 1933; *Chem. Abs.*, 1934, 28, 272.

<sup>129</sup> H. Plauson, German P. 560,260, 1931; *Chem. Abs.*, 1933, 27, 1220.

<sup>130</sup> British P. 333,298, 1928, to Bakelite Ges.; *Chem. Abs.*, 1931, 25, 611.

<sup>131</sup> French P. 670,000, 1929, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 1906.

<sup>132</sup> L. Lilienfeld, U. S. P. 1,991,810, Feb. 19, 1935; *Chem. Abs.*, 1935, 29, 2264. British P. 368,772, 1930; *Brit. Chem. Abs. B.*, 1932, 688. French P. 724,345, 1931; *Chem. Abs.*, 1932, 26, 4934.

<sup>133</sup> H. Spindler, French P. 637,051, 1928; *Chem. Abs.*, 1929, 23, 679.

<sup>134</sup> G. Walter, British P. 359,522, 1930; *Brit. Chem. Abs. B.*, 1932, 32.

<sup>135</sup> T. G. Levi, *Gazz. chim. ital.*, 1930, 60, 809; *Brit. Chem. Abs. A.*, 1930, 896.

<sup>136</sup> L. J. Roll and R. Adams, *J.A.C.S.*, 1932, 54, 2494.

<sup>137</sup> K. v. Auwers and E. Frese, *Ber.*, 1926, 59, 543.

Zaucker.<sup>138</sup> The polyamides of polycarboxylic acids (e.g., of adipic, suberic, diglycolic, hydrazine dicarboxylic or ethylenediamine-N,N'-dicarboxylic acid) can be condensed with formaldehyde (or related substances) to form resinous materials.<sup>139</sup> Christopher<sup>140</sup> prepared an adhesive by adding water to a powdered mixture of casein, biuret, cyanuric acid and formaldehyde. Cyanuric acid may be condensed with formaldehyde in water or organic solvents to give resinous products.<sup>141</sup>

Formaldehyde was used by Christopher and Beukelaer<sup>142</sup> to render glue or gelatin insoluble, and the product was then returned to a soluble form by the addition of urea. Lefebure<sup>143</sup> mixed water-soluble urea-formaldehyde condensation products, free from strong acids, with water-soluble salts of alginic acid and obtained compositions capable of forming stable solutions. Acetic acid or phenol are added to the mixture, and the products are used for paints, varnishes and for impregnating. Coloring matter incorporated with a urea-formaldehyde composition was used by the same investigator,<sup>144</sup> in the manufacture of decorated paper.

Substances having both waxy and resinous properties were prepared by Pungs and Stade<sup>145</sup> by combining crude or refined montan wax with urea-formaldehyde resins.

The reaction of urea with formaldehyde in the presence of zinc chloride gives a stable, syrupy, clear liquid suggested for use as an adhesive, coating or sizing. The method of preparation is as follows: 50 pounds of zinc chloride are dissolved in 275 pounds of 37 per cent formalin and 100 pounds of urea added.<sup>146</sup>

#### PRODUCTS WITH CELLULOSE DERIVATIVES

An aldehyde-urea condensation product may be added to an aqueous solution of a water-soluble alkyl cellulose (methyl cellulose), producing films or filaments on the removal of water.<sup>147</sup> The film formation is accelerated by heating or by exposure to ultraviolet light. A composition for ornamenting fabrics, yarns or paper, consisting of 15-60 per cent of a cellulose derivative with 40-85 per cent of the syrupy, intermediate condensation product of an aldehyde and urea or thiourea, was developed by Heynert and Lucius.<sup>148</sup> From 1 to 2 per cent of boric, lactic or phosphoric acid is added, together with mineral fillers, pigments and dyes. A urea-formaldehyde resin mixed with cellulose derivatives is used as a reinforcement coating for fragile glass or ceramic articles.<sup>149</sup>

An oxidation product of paraffin wax with nitric acid is esterified with butyl alcohol, and the resulting ester serves as a plasticizing and softening agent for lacquers, films and plastics containing cellulose derivatives, urea-aldehyde reaction products and other resins.<sup>150</sup>

<sup>138</sup> M. Bögemann and E. Zaucker, German P. 575,114, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3483.

<sup>139</sup> French P. 764,215, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5693.

<sup>140</sup> E. F. Christopher, Canadian P. 336,140, 1933, to Industrial Patents Corp.; *Chem. Abs.*, 1934, 28, 1824. Cf. A. Beuteli, French P. 755,147, 1933; *Chem. Abs.*, 1934, 28, 1486.

<sup>141</sup> British P. 420,525, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1935, 161. French P. 769,919, 1934; *Chem. Abs.*, 1935, 29, 525.

<sup>142</sup> E. F. Christopher and F. L. de Beukelaer, U. S. P. 1,895,447, Jan. 31, 1933, to Swift & Co.; *Chem. Abs.*, 1933, 27, 2597.

<sup>143</sup> V. Lefebure, British P. 386,328, 1933; *Chem. Abs.*, 1933, 27, 4432.

<sup>144</sup> V. Lefebure, British P. 265,334, 1925; *Brit. Chem. Abs. B.*, 1927, 296.

<sup>145</sup> W. Pungs and W. Stade, German P. 540,361, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1813.

<sup>146</sup> A. H. Bowen and T. W. Dike, U. S. P. 1,992,180, Feb. 26, 1935, to I. F. Laucks, Inc.; *Chem. Abs.*, 1935, 29, 2628. British P. 421,942, 1935; *Chem. Abs.*, 1935, 29, 3751.

<sup>147</sup> British P. 308,284, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 239. French P. 85,939, 1928, addn. to 615,876; *Chem. Abs.*, 1930, 24, 4155. G. Balle and K. Sponsel, German P. 542,287, 1927, addn. to 527,197, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2317.

<sup>148</sup> F. A. H. Heynert and F. Lucius, British P. 376,540, 1932; *Chem. Abs.*, 1933, 27, 4102.

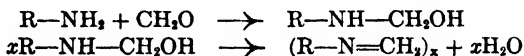
<sup>149</sup> British P. 345,758, 1930, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B.*, 1931, 541.

<sup>150</sup> British P. 395,340, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 483.

## Chapter 33

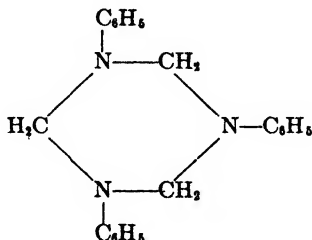
### Amine-Aldehyde Resins

The general reaction between formaldehyde and primary and secondary amines entails the formation of methylolamines, which are unstable and lose water, forming higher products derived from methyleneamines.

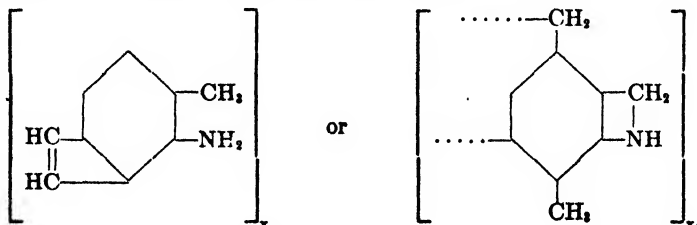


Even ammonia at low temperatures forms trimethylolamine, which changes readily to hexamethylenetetramine. Under the influence of an alumina catalyst, however, pyridine was the main product of the interaction of ammonia with mixtures of acetaldehyde and acetaldehyde.<sup>1</sup>

The condensation of aniline and formaldehyde follows the general reaction, anhydroformaldehydeaniline,  $(\text{C}_6\text{H}_5\text{N=CH}_2)_x$ , being formed. This is a six-membered ring compound of the structure



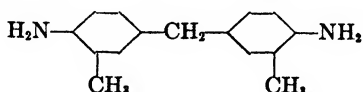
A higher polymer of the same empirical formula,  $\text{C}_7\text{H}_7\text{N}$ , is formed at the same time. In the presence of condensing agents, however, it is probable that formaldehyde reacts with the aromatic nucleus as well. For example, by using a mixture of concentrated sulphuric acid and acetic acid, or preferably 10 per cent sulphuric acid, Kroneberg<sup>2</sup> obtained from o-toluidine and formaldehyde a polymeric compound, to which he assigned the questionable structures



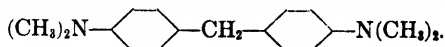
<sup>1</sup> A. E. Chichibabin and M. P. Oparina, *J. Russ. Phys.-Chem. Soc.*, 1924, 54, 601; *J.C.S.*, 1924, 126(1), 313. See also A. E. Chichibabin, *J. prakt. Chem.*, 1924, 107, 122; *Chem. Abs.*, 1924, 18, 1666.

<sup>2</sup> A. M. Nastyukov and P. M. Kroneberg, *J. Russ. Phys.-Chem. Soc.*, 1912, 44, 1200; *Chem. Abs.*, 1913, 7, 933. P. M. Kroneberg, *J. Russ. Phys.-Chem. Soc.*, 1916, 48, 305; *Chem. Abs.*, 1917, 11, 532.

When the product was distilled, some diaminoditolylmethane, reminiscent of certain



of the phenol-formaldehyde intermediates, was obtained. This does not show whether the diphenylmethane structure is actually present in the original product, or is formed during the distillation. The nuclear combination of formaldehyde is probable, since it is known that dimethylaniline and formaldehyde in the presence of hydrochloric acid form p,p'-tetramethyldiaminodiphenylmethane,



Researches, on the condensation of aromatic amines with formaldehyde in media containing acid, by Eisner and Wagner<sup>a</sup> have led to the isolation of several products of the amine-aldehyde reaction. The interaction of formaldehyde and p-toluidine was studied under conditions insuring a minimum formation of resinous higher-condensation products. The condensation was effected at or below room temperature in the presence of an excess of dilute hydrochloric acid, using slightly more than 1 equivalent of a 37 per cent formaldehyde solution. Final separation of the resultants of the reaction yielded a small amount of resinous material, a base ( $C_{24}H_{27}ON_3$ ) melting at 140°C., a base ( $C_{17}H_{18}N_2$ ) melting at 135°C and an additional base ( $C_{16}H_{18}N_2$ ) melting at 162.5°C. which was identified as 3-p-tolyl-6-methyl-3,4-dihydroquinazoline. A steam-volatile oil obtained during the course of the experiment was found to contain p-toluidine, methyl-p-toluidine and dimethyl-p-toluidine which latter compound was unexpected. The effect of increasing amounts of formaldehyde on the composition of this steam-volatile liquid was studied in order to explain the formation of the dimethyl-p-toluidine, and the results are shown in Table 33.

TABLE 33.—*Methylation of p-Toluidine Hydrochloride by Formaldehyde.*

Composition of steam-volatile products

Molar Ratio $CH_2O:C_7H_7N$	p-Toluidine %	Methyl-p- toluidine %	Dimethyl-p- toluidine %	Amine-H replaced by $CH_3$ %
1 0	68	27	0	2 3
1 5	3	20	77	7.7
2 0	0	0	100	6 7
2 5	0	0	100	8 5
5 0	0	0	100	9 1

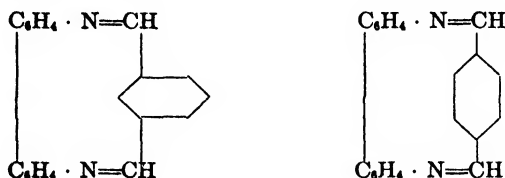
The effect of increase in the proportion of formaldehyde was not so much an increase in the number of p-toluidine molecules methylated as an increase in the thoroughness of methylation of the molecules affected.

Wagner<sup>a</sup> heated aromatic amines (n-propylaniline, n-butaniline, isoamylaniline, o-toluidine and m-toluidine) and a half equivalent of formaldehyde in acid solution. The resins obtained were found in some cases to be stable bases distillable *in vacuo*, but the quantities obtained were too small to permit further study. In the aniline reaction, a condensation product boiling at 329-334°C. (at 1-2 mm. pressure) was formed, and its nitrogen content (13.75 per cent) and molecular weight (351) indicated a mixture of trinuclear and tetranuclear bases (e.g.,  $C_{30}H_{31}N_3$  and  $C_{27}H_{28}N_4$ ).

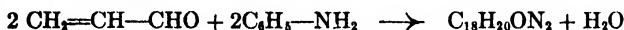
<sup>a</sup> A. Eisner and E. C. Wagner, *J.A.C.S.*, 1934, 56, 1938.

<sup>a</sup> E. C. Wagner, *J.A.C.S.*, 1934, 56, 1944.

Benzidine reacts with terephthalaldehyde and isophthalaldehyde to form high-melting, insoluble substances. Adams, Bullock and Wilson<sup>6</sup> assigned the following structures to these products.



Mann<sup>8a</sup> found that aniline and acraldehyde reacted at 0°C. forming a resinous product according to the equation



With p-toluidine an analogous compound of the formula  $\text{C}_{20}\text{H}_{24}\text{ON}_2$  was obtained. The aniline derivative was a white amorphous precipitate, which rapidly developed a deep red color owing to oxidation. Littman and Brode<sup>9</sup> represented the condensation of secondary amines with benzaldehyde by the following equation



A further example of the isolation of definite compounds from amine-aldehyde condensations is furnished by the reaction between benzidine and formaldehyde, studied by Kondo and Ishida.<sup>7</sup> They found that dihydroxymethylenebenzidine was obtained as a grayish-white amorphous powder, sintering at 260° C. and melting at 271-272°C., by adding 30 cc. of 35 per cent formaldehyde solution to 10 grams of benzidine dissolved in 200 cc. of absolute alcohol.

Schiff bases are condensation products of aromatic aldehydes and primary amines. Wagner<sup>8</sup> has carried out reduction studies on Schiff's bases of the simple type  $\text{RCH}=\text{NR}'$  (azomethines) to gain evidence of their structure. Methylene-p-aminophenol was prepared<sup>9</sup> in alkaline or neutral solution by the condensation of p-aminophenol and formaldehyde. Made in the presence of alkali, this compound is a white, amorphous powder that darkens and becomes resinous in air. Cryoscopic determinations of the molecular weight of methylene-p-aminophenol suggest that it can exist wholly or largely monomeric, but the degree of its polymerization is indefinite. While investigating the catalytic hydrogenation of cyano derivatives, Rupe and Pieper<sup>10</sup> reduced ethyl benzylideneacyanoacetate obtaining two products, the half aldehyde of benzylmalonic acid and an amino acid ( $\alpha$ -benzyl- $\beta$ -amino-propionic acid). The two products condense together to form a Schiff base, which is obtained as a resin and can be separated into its components with mineral acid. Miller and Wagner<sup>11</sup> found that the lower normal aliphatic aldehydes other than formaldehyde when condensed with aniline gave the di-imine, the simple azomethine,  $\text{C}_6\text{H}_5\text{N}=\text{CHR}$ , changing to the dimeric molecule, repre-

<sup>6</sup> R. Adams, J. F. Bullock and W. C. Wilson, *J.A.C.S.*, 1923, 45, 521.

<sup>8a</sup> F. G. Mann, *J.C.S.*, 1922, 121, 2178; see also H. Schiff, *Ann. Suppl.*, 1864, 3, 358.

<sup>9</sup> J. B. Littman and W. R. Brode, *J.A.C.S.*, 1930, 52, 1655.

<sup>7</sup> H. Kondo and S. Ishida, *J. Pharm. Soc. Japan*, 1922, 489, 979; *Chem. Abs.*, 1923, 17, 1456.

<sup>8</sup> E. C. Wagner, *J.A.C.S.*, 1932, 54, 660. L. Musago and M. Pepe (*Gazz. chim. ital.*, 1931, 61, 910; *Chem. Abs.*, 1932, 26, 2737) obtained a black resinous substance by reducing furfurylidene- $\beta$ -naphthylamine with magnesium and extracting the oily residue.

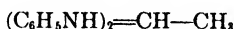
<sup>9</sup> German P. 68,707, 1892, to Ges. für chem. Ind., Basel; *Chem.-Zentr.*, 1893, 2, 551.

<sup>10</sup> H. Rupe and B. Pieper, *Helv. Chim. Acta*, 1929, 12, 637; *Chem. Abs.*, 1929, 23, 4463.

<sup>11</sup> J. G. Miller and E. C. Wagner, *J.A.C.S.*, 1932, 54, 3693. The behavior of isobutyraldehyde is referred to by E. Friedling and G. Mossler (*Monatsh.*, 1901, 22, 460; *J.C.S.*, 1901, 80 (1), 641) and that of isovaleraldehyde by A. Eibner and G. Purucker (*Ber.*, 1900, 33, 3658). Hexahydrobenzaldehyde reacts with ammonia to form the imine almost exclusively which then polymerizes to give a stable compound,  $(\text{C}_6\text{H}_{11}\text{CH}=\text{NH})_x$ . (C. F. Winans and H. Adkins, *J.A.C.S.*, 1933, 55, 2058.)



sented, e.g., by the compound,  $C_6H_5NH-CH(CH_3)-CH_2CH=N-C_6H_5$ , due to an aldol-like condensation. These products were oils. By condensing pure aniline and pure acetaldehyde, with chilling, ethylidene-dianiline



a white crystalline solid, was formed. In their research on the character of nitrogen-containing synthetic resins (e.g., Schultz's bases), Eibner and Koch<sup>12</sup> added 18 g. of acetaldehyde in 180 cc of water to a solution of aniline hydrochloride (64 g.) in water (640 g.) at 0°C. If the reaction mixture is neutralized at once, 10 per cent of a resin (which melts at 126°C. when crystallized from ether and is identical with Eckstein's base) is precipitated. If, however, the mixture is allowed to stand for 4 weeks without neutralization, an alcohol-soluble resin (Schultz's base) melting at 175-185°C. is formed. Schultz's base proved to be a mixture of two compounds. Petroleum ether precipitates from an ether solution a resin melting at 175-185°C. and ether precipitates from a benzene solution a resin which sinters at 250°C. Schultz's bases are the result of a polymerization of Eckstein's base with the removal of the aniline group adjacent to the double bond. In the paint industry Schultz's bases are of little value because they swell, discolor, are brittle and prevent hardening of the paint film.

Levi<sup>13</sup> has carried out an extensive investigation of the condensation reaction of aminophenols and aldehydes with a view to using the products in the rubber industry. A number of new substances were described, some being crystalline and others amorphous, though no tests of their effect on rubber are recorded. The reaction was carried out in water solution, with the materials suspended in water, if insoluble, or between the aldehyde and a hydrochloric acid salt of the aminophenol in the presence of ammonium acetate. Glazer and Frisch<sup>14</sup> have studied the condensation products from acid amides and aldehydes either by melting the reactants together or by allowing them to react in alcoholic solution in the presence of hydrochloric acid. In this case, also, definite crystalline products of known composition were obtained.

Tar and resin formation has been recorded in other reactions, however. In condensing diethylaniline with phosphorus trichloride, Bourneuf<sup>15</sup> obtained a resinous product, although a similar treatment of dimethylaniline gave pure compounds. The sodium compound of N-benzylideneglycylglycine resinifies quickly on exposure to air, becoming red in color.<sup>16</sup> A yellow amorphous mass was secured by Reissert and Händler<sup>17</sup> when an ice-cold solution of isatin, which was acid to Congo red, was treated with formaldehyde and an excess of mineral acid. Klason<sup>18</sup> observed the formation of tars in the reaction between paraldehyde and  $\beta$ -naphthylamine hydrochloride. Pyman<sup>19</sup> reported much resin formation in the condensation of glyoxaline with formaldehyde. The reaction was effected at 125-135°C. in a sealed tube with 40 per cent formaldehyde. On heating together aniline and  $\beta$ -chlorobutaldehyde diethylacetal in a sealed tube at 220°C. for 5 hours, a dark brown oil was formed, which on fractionation gave a large amount

<sup>12</sup> A. Eibner and E. Koch, *Z. angew. Chem.*, 1926, 39, 1514; *Chem. Abs.*, 1927, 21, 2808.

<sup>13</sup> T. G. Levi, *Garz. chim. ital.*, 1929, 59, 544; *Chem. Abs.*, 1930, 24, 351.

<sup>14</sup> E. Glazer and S. Frisch, *Arch. Pharm.*, 1928, 265, 103; *Brit. Chem. Abs. A.*, 1928, 652.

<sup>15</sup> M. Bourneuf, *Bull. soc. chim.*, 1923, 33, 1808; *Chem. Abs.*, 1924, 18, 977.

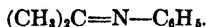
<sup>16</sup> O. Gerngross and E. Zühlke, *Ber.*, 1924, 57, 1482; *Chem. Abs.*, 1925, 19, 242.

<sup>17</sup> A. Reissert and A. Händler, *Ber.*, 1924, 57, 989; *Chem. Abs.*, 1924, 18, 3058.

<sup>18</sup> P. Klason, *Ber.*, 1925, 58, 1763; *Chem. Abs.*, 1926, 20, 399. The tar remaining after the distillation of  $\alpha$ -naphthylamine in *vacuo* was analyzed by V. Lenkhold and E. Ostroumov (*J. Chem. Ind. (Russia)*, 1929, 6, 216; *Chem. Abs.*, 1930, 24, 3009). Iron oxides, lubricating oil, 6 per cent of  $C_{10}H_7NH_2$ , and traces of  $\alpha$ - and  $\beta$ -naphthol were found.

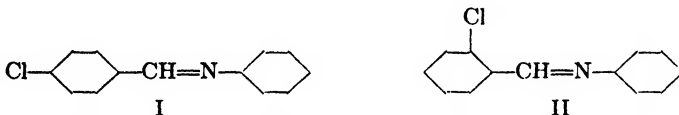
<sup>19</sup> F. L. Pyman, *J.S.C.I.*, 1927, 46, 1151.

of tar.<sup>30</sup> Gray<sup>31</sup> found that only tarry products were produced when d-glutamic acid and diphenylamine reacted at 240°C.; at lower temperatures, 1,2-pyrrolidone-5-carboxyanilide formed. Knoevenagel<sup>32</sup> has reported the resinification of the dimer of acetone-anil,



In a study of Döbner's reaction<sup>33</sup> between aromatic aldehydes, amines and pyruvic acid, Carrara<sup>34</sup> obtained high yields of resins and low yields of quinoline-γ-carboxylic acids. For instance, by adding dropwise 40 parts of pyruvic acid to a boiling mixture of aniline (67 parts) and benzaldehyde (76 parts) in an excess of ethyl alcohol and refluxing for 5 hours, 100 parts of a viscous, brown resin are given. Levine and Wehmhoff<sup>35</sup> have described a condensation product, deep red in color, of o-aminophenol and oxalic acid. This substance melts at 271-272°C. and decomposes when heated a few degrees above its melting point giving carbon dioxide and a tarry substance which could not be purified. Increased heating entirely decomposes the red product into carbon dioxide, water, o-aminophenol and an unidentified substance melting above 300°C. β-Ethoxy-acrolein-acetal was reported by König and Seifert<sup>36</sup> to give a soft resin when reacted with dimethylaniline in the presence of zinc chloride.

Electrolytic reduction of o-, m-, and p-chlorobenzylidene anilines yields the corresponding chlorobenzyl anilines, together with a resin. The amount of resin formed diminishes as the substituent group advances towards the center of the molecule. Thus I yields more resin than II.



Electrolytic reduction of the tolylidene toluidines also yields resins. Less resin is formed in this case when the substituting groups are evenly distributed in the two benzene nuclei.<sup>37</sup>

Bytebier,<sup>38</sup> in preparing diaminodiphenylmethane from aniline and formaldehyde, observed that under certain conditions synthetic resins, similar in appearance to rosin, were formed. These substances were soluble in the organic solvents used in the paint industry, and also in warm acid solutions, showing them to be basic in character. A resin of this sort was obtained, e.g., on pouring 1 molecular proportion of formaldehyde at 0-5°C. into a mixture of 1.13 mols of hydrochloric acid, and 2.25 mols of aniline. After 1 hour the mixture is heated to 90-95°C. and maintained at this temperature for 10 hours, the resin being precipitated on making the solution alkaline with caustic soda.

In the case of the reaction between aldehydes and amines the nature of the product is controlled very largely by the conditions. The character of the products formed in the reaction of formaldehyde with diphenylamine depends on the relative proportions of the reactants.<sup>39</sup> An excess of diphenylamine favors the

<sup>30</sup> F. A. Mason, *J.C.S.*, 1925, 127, 1035. See also O. Gerngross and M. Dunkel, *Ber.*, 57, 739; *Chem. Abs.*, 1924, 18, 2386.

<sup>31</sup> W. H. Gray, *J.C.S.*, 1928, 1267.

<sup>32</sup> E. Knoevenagel, *Ber.*, 1928, 56, 2414; *Chem. Abs.*, 1924, 18, 1299.

<sup>33</sup> O. Döbner and M. Giesecke, *Ann.*, 1887, 242, 290; *J.C.S.*, 1888, 54, 300. O. Döbner, *Ber.*, 1887, 20, 277; *J.C.S.*, 1887, 52, 504. See also K. Garsarolli-Thurnlackh, *Ber.*, 1899, 32, 2274; *J.C.S.*, 1899, 76, 940.

<sup>34</sup> G. Carrara, *Gazz. chim. ital.*, 1928, 58, 309; *Chem. Abs.*, 1929, 23, 891.

<sup>35</sup> A. A. Levine and L. Wehmhoff, *J.A.C.S.*, 1929, 51, 1243.

<sup>36</sup> W. König and K. Seifert, *Ber.*, 1934, 67, 2112.

<sup>37</sup> H. Law, *J.C.S.*, 1912, 101, 154.

<sup>38</sup> A. Bytebier, *Rev. chim. ind.*, 1926, 35, 365; *Chem. Abs.*, 1927, 21, 1020.

<sup>39</sup> D. Craig, *J.A.C.S.*, 1933, 55, 3723.

formation of a definite compound,  $\text{CH}_2(\text{C}_6\text{H}_4\text{NHC}_6\text{H}_5)_n$ , whereas an excess or even an equimolecular proportion of formaldehyde results in the formation of resins. It is possible in some cases to isolate definite compounds, but in other circumstances only the ill-defined resin is formed. It can be stated quite generally that the resinous substances are either higher polymers, or represent a greater degree of condensation than that in the identifiable derivatives

Resin formation in these reactions is favored by (1) higher temperature and greater duration of reaction; (2) excess of the aldehyde and (3) the presence of a catalyst, especially an acid. In the following account of some of the chief amine-aldehyde resins little reference is made to the probable composition. It will be understood that in practically every case they represent the product of a more or less complex condensation reaction of the type already outlined.

#### RESINS FROM ANILINE AND FORMALDEHYDE

The production of resins of this type<sup>30</sup> has been developed largely during the last ten years. An acid is used in most cases as a condensing agent, a feature which offers a parallel with the production of resins from aldehydes and urea.<sup>31</sup>

Böhler<sup>32</sup> prepared a resin by heating anhydroformaldehydeaniline to a temperature of 130-140°C. for 10 to 12 hours. A dense cloud of white vapors is given off during the reaction. The presence of aniline during the distillation is desirable as it appears to facilitate the reaction and to improve the solubility of the resin in benzene or alcohol. Slight amounts of acids or alkalis may be added to the reaction mixture. This synthetic resin is said to have the property of increasing the solubility of difficultly-soluble natural or synthetic resins and to improve their qualities otherwise. Soane<sup>33</sup> obtained a resilient composition for printers' rollers by treating a water-containing mixture of glue and glycerol with aniline-formaldehyde condensation products. Berend<sup>34</sup> prepared these substances by dissolving glue in equal parts of phenol and glycerol and adding shellac, dissolved in aniline and homogenized by heat with paraformaldehyde. The temperature of the mixture is raised to 70°C. and glycerol-formaldehyde or additional paraformaldehyde is added. The tough mass which results is molded before solidifying. In the course of preparation of anhydroformaldehydeaniline from aniline and formaldehyde Eberhardt and Welter<sup>35</sup> obtained some polymerized anhydro compounds and resinous bodies.

Since 1928, investigators have introduced a number of adaptations and modifications of the general method of condensing aromatic amines with formaldehyde. One molecular proportion of aniline may be condensed with 1 mol of formaldehyde in the presence of at least 0.25 of the equivalent amount of hydrochloric acid, calculated on the basis of the amine. The resinous material precipitates as soon as the acid is neutralized. After removal of the acid, the resin (m. p., 180-200°C.) is dried, pulverized and then hardened with more formaldehyde.<sup>36</sup> The density of the porous product of such a condensation is increased by heat and pressure, e.g., by heating for about 1 hour at 150°C. and 100 atmospheres pres-

<sup>30</sup> For a review of amine-aldehyde synthetic resins see A. Dolus, *Rev. chim. ind.*, 1923, 32, 185, 211; *Chem. Abs.*, 1923, 17, 3796. See also *British Plastics*, 1931, 292.

<sup>31</sup> See Chapter 26.

<sup>32</sup> C. Böhler, *Kunststoffe*, 1921, 118, 142; German P. 335,984, 1917; *J.S.C.I.*, 1921, 40, 666A.

<sup>33</sup> C. E. Soane, U. S. P. 1,223,745, Apr. 24, 1917; *Chem. Abs.*, 1917, 11, 1893.

<sup>34</sup> L. Berend, British P. 4154, 1909, to Commercial Products Co., Ltd.; *Chem. Abs.*, 1910, 4, 2581.

<sup>35</sup> C. Eberhardt and A. Welter, *Ber.*, 1894, 27, 1805; *J.C.S.*, 1894, 66 (1), 451.

<sup>36</sup> Swiss P. 141,223 and 141,224, 1928, to Soc. anon. pour l'ind. Chim. à Bâle; *Chem. Abs.*, 1931, 25, 1046. British P. 342,325, 1928; *Chem. Abs.*, 1931, 25, 5305. British P. 342,767, 1929; *Brit. Chem. Abs.* B. 1'31, 503. German P. 559,324, 1928; *Chem. Abs.*, 1933, 27, 818. French P. 683,914, 1929; *Chem. Abs.*, 1930, 24, 5119. Swiss P. 154,831, 1931; *Chem. Abs.*, 1933, 27, 1113. German P. 561,157, 1929; *Chem. Abs.*, 1933, 27, 1220. British P. 414,404, 1933; *Brit. Chem. Abs.* B, 1934, 873.

sure.<sup>37</sup> The hydrochloric acid is eliminated by treatment with a 3 per cent sodium hydroxide solution. The heat and pressure treatment increases the specific gravity of the resin from 0.6 to about 1.0<sup>38</sup> and improves the working properties and insulating capacity of the product. The compression of this condensation product may also be carried out in the presence of fluxes, such as a fusible non-hardening phenol-formaldehyde condensation product.<sup>39</sup> A filling material (sawdust) may be impregnated with the amine-aldehyde condensation product before eliminating the acid. The condensation products are afterwards precipitated in the filling material by adding an agent to neutralize the acid (an acid binding agent), and the final product is washed, dried and hot-molded, hardening agents being added if required.<sup>40</sup> The following example illustrates the use of these bodies in conjunction with a filler.<sup>41</sup> Aniline is condensed with formaldehyde in presence of hydrochloric acid. After being kept at 30°C. for half an hour, the resin is precipitated by being run into sodium hydroxide solution, and is then washed free from electrolytes. A fibrous or powdery filler (wood flour, asbestos or cotton) is mixed with the moist condensation product (before or after washing) and the mixture is eventually hot-molded. Aldehydic hardening agents, fluxing agents or coloring materials may be incorporated before molding.<sup>42</sup> Resins similarly prepared may be applied to supports and then subjected to heat and pressure.<sup>43</sup> A resin to which fillers or plasticizing agents may be added is formed by the reaction of a primary aromatic amine with more than 2 mols of formaldehyde and a large amount of strong mineral acid, at a high temperature.<sup>44</sup> The product is washed, dried and compressed by heating under pressure. Using filling materials (e.g., sulphite pulp, leather chips or cellulose) it is possible to make paper-like material (cardboard) and imitation leather by this process.<sup>45</sup> Insulators of the condenser type, for the terminals of high-tension transformers, are obtained by molding and compressing together an assemblage of metal sheets coated with the product of the acid condensation of aniline and formaldehyde.<sup>46</sup>

The infusible (hardened) and insoluble condensation products obtained from an aromatic amine and more than 1 molecular proportion of an aldehyde may be converted into fusible and soluble products by heating them with a fusible aldehyde condensation product of phenol, or with a non-aldehydic fusible synthetic resin as that from glycerol-phthalic acid.<sup>47</sup> As an example, aniline is treated with more than 1 mol of formaldehyde in the presence of hydrochloric acid, and a

<sup>37</sup> British P. 283,965, 1927, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1928, 22, 4213.

<sup>38</sup> British P. 284,589, 1927, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1928, 22, 4740. French P. 646,921 and 646,922, 1928; *Chem. Abs.*, 1929, 23, 2257.

<sup>39</sup> French P. 37,841, 1929, addn. to 646,922, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1931, 25, 4673. German P. 562,440, 1929; *Chem. Abs.*, 1933, 27, 818. French P. 37,496, 1929, addn. to 646,922, 1928; *Chem. Abs.*, 1931, 25, 2531. British P. 342,730, 1928; *Chem. Abs.*, 1931, 25, 5585.

<sup>40</sup> French P. 37,696, 1929, addn. to 646,922, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1931, 25, 4673. German P. 562,518, 1931, *Chem. Abs.*, 1933, 27, 1220. German P. 562,943, 1929; *Chem. Abs.*, 1933, 27, 1113. British P. 342,723, 1929; *Brit. Chem. Abs. B.*, 1931, 503.

<sup>41</sup> British P. 368,300, 1930, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs. B.*, 1932, 519. See also British P. 371,481, 1931; *Brit. Chem. Abs. B.*, 1932, 688. German P. 599,488, 1934; *Chem. Abs.*, 1934, 28, 5604.

<sup>42</sup> See British P. 342,825 and 342,326, 1929, addns. to British P. 284,589, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs. B.*, 1931, 405. Swiss P. 142,936, 1928; *Chem. Abs.*, 1931, 25, 2253. Swiss P. 144,226, 1928; *Chem. Abs.*, 1931, 25, 4096. Swiss P. 146,009, 1928; *Chem. Abs.*, 1932, 26, 267. French P. 728,916, 1931; *Chem. Abs.*, 1932, 26, 6166. German P. 565,702, 1930; *Chem. Abs.*, 1933, 27, 2541.

<sup>43</sup> British P. 371,481, 1930, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1933, 27, 3095.

<sup>44</sup> French P. 757,038, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 2556. Swiss P. 163,020, 1933; *Chem. Abs.*, 1934, 28, 2860. German P. 598,061, 1934; *Chem. Abs.*, 1934, 28, 5604. British P. 415,555, 1933; *Brit. Chem. Abs. B.*, 1934, 972.

<sup>45</sup> Swiss P. 154,520, 1930, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1933, 27, 1113. French P. 726,133, 1931; *Chem. Abs.*, 1932, 26, 4925. British P. 368,300, 1930; *Chem. Abs.*, 1933, 27, 2321.

<sup>46</sup> G. E. Haefely, British P. 323,343, 1928, to Micanite & Insulators Co. Ltd.; *Chem. Abs.*, 1930, 24, 3067. For the application of dielectric-loss measurements to aniline-formaldehyde resins see R. Köhler, *Kolloid-Z.*, 1932, 59, 143; *Chem. Abs.*, 1932, 26, 4235.

<sup>47</sup> British P. 343,882, 1928, Swiss P. 146,375, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 324. British P. 372,075 and 372,076, 1931; *Brit. Chem. Abs. B.*, 1932, 688. German P. 565,634, 1929; *Chem. Abs.*, 1933, 27, 2591. See also A. Gams and K. Frey, U. S. P. 1,909,093, Apr. 23, 1935, to Ciba Products Corp.

solution of a phenol-formaldehyde resin is added. The mixture is then neutralized with sodium carbonate, heated and the resin filtered off. The added substance here plays the part of a fluxing agent. Conversely, the fusible condensation products prepared by the reaction of formaldehyde and primary amines in the presence of nearly equivalent quantities of acid may be made infusible by the action of fresh amounts of aldehydes at temperatures less than 140°C. The final hardening is done at higher temperatures under pressure.<sup>48</sup> The condensation product from amines and aldehydes has been suggested for making joints tight against liquids, vapors and gases.<sup>49</sup>

By dissolving the condensation product from an aromatic amine and formaldehyde, in presence of almost an equivalent quantity of acid, together with aldehydes or agents liberating aldehydes in the common solvents, solutions are obtained which are used for the production of insoluble coatings stable to heat, and which have a high mechanical and chemical resistance.<sup>50</sup> Chlorohydrins are employed as solvents for the infusible condensation products. Additions of softening agents, pigments, cellulose derivatives, fillers, rubber, resins and diluents may be made to the solutions, which are proposed for use as lacquers.<sup>51</sup> Glycol chlorohydrin or epichlorohydrin, mixed with swelling agents including cyclohexanone, ethyl lactate and chloroform, are generally used, solution being accelerated by heating.<sup>52</sup> Light<sup>53</sup> condensed equimolecular proportions of formaldehyde and a primary aromatic amine in the presence of an acid for 5 minutes at 70°C. and, subsequently, several minutes at 90°C. Further heat-treatment converts the resinous residue into hard, transparent, pale yellow to orange resins, which may be made opaque by boiling with water.

An oil-modified resin is obtained by heating a drying oil (e.g., tung oil) with aniline and treating with anhydroformaldehydeaniline. The product is rendered thermosetting by reaction with formaldehyde.<sup>54</sup>

#### IMPREGNATION OF PULP WITH ANILINE-FORMALDEHYDE RESINS

Kienle and Scheiber<sup>54</sup> carried out the condensation of an aromatic amine (aniline, 1 mol) with an aldehyde (formaldehyde, 1 mol) in hydrochloric acid solution at 40°C. and added a fibrous pulp, with or without a filling material, to the clear acid liquid. After stirring for 1 hour to saturate the pulp, the mixture is diluted with water, and an alkali (lime) added to neutralize the acid and to precipitate the resin which is flocculated at 60°C. The stock is beaten and sheets formed from the stock on a paper-making machine, several such sheets being superimposed. Molding of the product is carried out at 150°C. and at a pressure greater than 1000 lb. per square inch. The flocculated product may be diluted to a consistency of about 1 per cent and formed into sheets, which are dried, calendered and heated under pressure. The following example gives some further details

<sup>48</sup> French P. 719,636, 1931, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 3946. French P. 719,574, 1931; *Chem. Abs.*, 1932, 26, 3886. French P. 749,962 1933; *Chem. Abs.*, 1934, 28, 665.

<sup>49</sup> Swiss P. 148,845, 1929, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1933, 27, 1113.

<sup>50</sup> French P. 719,929, 1931, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 3945. Swiss P. 153,498, 1930; *Chem. Abs.*, 1933, 27, 1220. German P. 564,525, 1930; *Chem. Abs.*, 1933, 27, 1220.

British P. 373,358, 1932; *Chem. Abs.*, 1933, 27, 4107.

<sup>51</sup> German P. 539,352 1929, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1932, 26, 1812.

Swiss P. 148,505, 1928; *Chem. Abs.*, 1932, 26, 4970.

<sup>52</sup> French P. 684,317, 1929, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1930, 24, 5518.

British P. 343,031, 1929; *Brit. Chem. Abs.* B, 1931, 503.

<sup>53</sup> L. Light British P. 275,725, 1926; *Chem. Abs.*, 1928, 22, 2475.

<sup>54</sup> British P. 424,536, 1934, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs.* B, 1935, 368.

<sup>55</sup> R. H. Kienle and W. J. Scheiber, British P. 352,140, 1930, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B, 1931, 852. See also R. H. Kienle, Canadian P. 323,673, 1932, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1932, 26, 4488. British P. 360,381 and 360,380, 1930, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 1220. R. H. Kienle and W. J. Scheiber, Canadian P. 323,670, 1932, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1932, 26, 4719.

of the process employed.<sup>55</sup> The initial condensation is carried out with a mixture of 15,000 lb. of water, 920 lb. of aniline, 990 lb. of 36 per cent hydrochloric acid and 912 lb. of 38.8 per cent formaldehyde, the ordinary paper mill beater serving as a reaction chamber. The reaction temperature is not allowed to rise above 40°C., and condensation is complete in an hour. The pulp is now added, a quantity of 100 lb., calculated on a dry weight basis, being the usual amount. After the pulp is saturated, the mixture is diluted with 10,000 lb. of water, and 420 lb. of lime, preferably as milk of lime, are added to neutralize the acid and precipitate the resin. The temperature is raised to 60°C., and the material is beaten to bring about an attachment of the resin flocculates to the fibers,<sup>56</sup> a step which may take from 2 to 40 hours, depending on the conditions and materials used. After heating, the stock is diluted to about 1 per cent and delivered into a paper-making machine, and the sheet pulp is dried, calendered and pressed. (See Fig. 115.) A resin prepared in a similar manner may be used on and around the interlocked fibers of a wet paper pulp which is built up in layers to form a

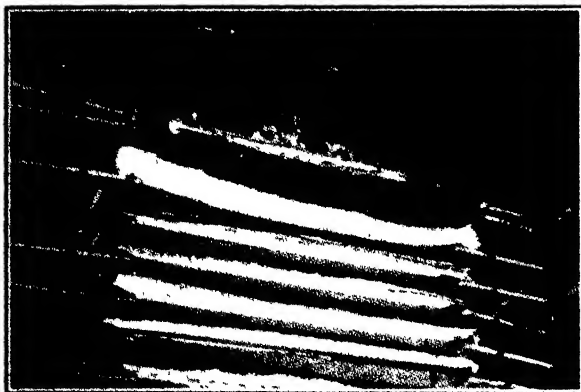


FIG. 115.

Part of Laminating Press  
for Heating and Curing  
Finished Sheets.

*Courtesy Modern Plastics*

laminated product. The mass is dried and molded under heat and pressure.<sup>57</sup> The molded material is an inert, infusible body of great mechanical strength, and with good insulating qualities. It is used in the manufacture of various articles such as laminated products, insulating tapes, gears, slot insulating materials, transformer spacers and refrigerator strips. Laminated tubes are prepared by impregnating paper with fusible, non-hardening resins of the anhydroaminobenzyl alcohol type (e.g., from formaldehyde and aniline hydrochloride) and making up in a tube-rolling machine.<sup>58</sup> This type of resin is also used as a binder in making lamellar masses.<sup>59</sup> The layers are impregnated with the resin and assembled by the action of heat and pressure. The anhydro-p-aminobenzyl alcohol binding agent is also mixed with fibers, and various articles are made from it by hot-pressing.<sup>60</sup> Kienle considers that the use of a strong alkali (caustic soda)

<sup>55</sup> R. H. Kienle and W. J. Scheiber, U. S. P. 1,812,749, June 30, 1931, to General Electric Co.; *Chem. Abs.*, 1931, 25, 5027. See also French P. 694,669, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 2013. French P. 38,868, 1930, addn. to 6'4,669; *Chem. Abs.*, 1932, 26, 1813.

<sup>56</sup> At elevated temperatures (40-100°C.) large particles of resin are produced which adhere to the pulp fibers. (W. J. Scheiber and P. F. Schlingman, British P. 363,683, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 1774.)

<sup>57</sup> R. H. Kienle and W. J. Scheiber, British P. 393,412, 1933, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 5910.

<sup>58</sup> British P. 405,491, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs.*, 1934, 331.

<sup>59</sup> G. P. Landt, British P. 419,901, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs.*, 1935, 111. French P. 754,100, 1933; *Chem. Abs.*, 1934, 28, 1153.

<sup>60</sup> Swiss P. 161,570, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 591.

to precipitate the resin leads to a product which does not lend itself readily to molding.<sup>61</sup> The product with sodium hydroxide lacks flow, which is a serious drawback when molding with fillers. To overcome this difficulty precipitation is carried out with calcium, barium, or magnesium hydroxide. An added advantage of the use of these agents is the production of more soluble salts on neutralization. Amine-aldehyde resins of greater fluidity are also prepared by replacing aniline with toluidines, diphenylamines, naphthylamines or benzidines.<sup>62</sup>

#### OTHER APPLICATIONS OF ANILINE-FORMALDEHYDE RESINS

Vacher<sup>63</sup> developed a method of preparing a resin of the type under consideration by heating together 100 parts of aniline and 90 parts of 40 per cent aqueous formaldehyde with 25 parts of a phenol (especially cresol) as a catalyst. Unreacted material is distilled off under reduced pressure (500 mm.) and the product on heating to 170°C. is converted into an infusible, insoluble resin. Molding may be combined with this heat treatment. Before the final treatment, the product melts between 50-80°C. to a liquid with approximately the viscosity of water, and it may be used in this state for impregnating, or, dissolved in an organic solvent, may be employed as a varnish. Vacher also utilizes acids, bases and salts as catalysts in addition to phenols. The final hardening of the resins may be carried out by heating in the presence of a hardening agent (hexamethylenetetramine).<sup>64</sup>

Anhydroformaldehyde compounds given by the condensation of salts of aromatic amines with resin acids or fatty acids of high molecular weight and formaldehyde were prepared by Berend<sup>65</sup> and may be used as substitutes for camphor and as solid solvents for nitrocellulose, in the manufacture of varnishes. For example, 80 g. of oleic acid are dissolved in 60 g. of aniline and warmed on a water-bath with 20 g. of paraformaldehyde until reaction ceases. An amorphous, yellowish-white mass, melting at 50°C., is obtained. The excess aniline is removed by boiling the product with water.

The use of aromatic amines other than aniline is recommended by Schlingman,<sup>66</sup> as giving an easily moldable resin. Benzidine and diphenylamine are mentioned in this connection, condensation with the aldehyde being carried out in acid solution and the condensation product precipitated with a base. The use of amines having a larger space arrangement in the molecule than aniline results in the formation of resinous compositions with increased flexibility and plasticity.

Anhydrous aldehydes or their solid polymers (2 mols), and aromatic amines (1 mol), may be condensed in the presence of a polybasic organic acid, particularly phthalic acid, in a solvent (benzene, alcohol or aniline).<sup>67</sup> The condensation of anhydrous formaldehyde and aniline may be effected in ethyl alcohol solution in the presence of phthalic acid and a contact substance such as stannic chloride.<sup>68</sup> The reaction product is subsequently hardened. The softening point

<sup>61</sup> R. H. Kienle, U. S. P. 1,878,527, Sept. 20, 1932, to General Electric Co.; *Chem. Abs.*, 1933, 77, 435. Allgem. Elekt. Ges., British P. 414,393, 1933, to Int. Gen. Electric Co.; *Brit. Chem. Abs.*, B, 1934, 897.

<sup>62</sup> French P. 38,433, 1930, addn. to 694,669, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 1144.

<sup>63</sup> F. Vacher, U. S. P. 1,873,799, Aug. 23, 1932, to Cont.-Diamond Fibre Co.; *Chem. Abs.*, 1932, 26, 6166. See also British P. 282,435, 1926, to Soc. anon. la fibre Diamond; *Chem. Abs.*, 1928, 22, 3792.

<sup>64</sup> French P. 644,075, 1927, to Soc. anon. la fibre Diamond; *Chem. Abs.*, 1929, 23, 1764.

<sup>65</sup> L. Berend, German P. 222,512, 1908; *Chem. Abs.*, 1910, 4, 2884.

<sup>66</sup> P. F. Schlingman, U. S. P. 1,982,486, Nov. 27, 1934, to General Electric Co.; *Chem. Abs.*, 1935, 29, 523. British P. 760,393, 1930, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 616. Canadian P. 328,264, 1932, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1933, 27, 1219.

<sup>67</sup> French P. 717,931 and 717,027, 1931, to Allgem. Elekt.-Ges.; *Chem. Abs.*, 1932, 26, 2880, 2931. Allgem. Elekt.-Ges., British P. 388,097, 1933, to Int. Gen. Electric Co., Inc.; *Chem. Abs.*, 1933, 27, 4701. H. Burmeister, German P. 593,444, 1934; *Chem. Abs.*, 1934, 28, 5694. German P. 600,831, 1934; *Chem. Abs.*, 1934, 28, 7564.

<sup>68</sup> French P. 722,634, 1931, to Allgem. Elekt.-Ges.; *Chem. Abs.*, 1933, 26, 4191. Allgem. Elekt.-Ges.,

of these aniline-formaldehyde resins is raised by restricting the amount of the phthalic acid to not more than 0.04 equivalent (relative to the amine) and by a subsequent heat treatment.<sup>69</sup> Molding substances may be manufactured in a single condensation step in the absence of solvents on heated mill rolls.<sup>70</sup> Wood flour, paraformaldehyde, aniline, phthalic acid and coloring matter are processed in a rubber mill at 120-140°C. producing compact sheets which may be further worked. Similarly,  $\alpha$ - or  $\beta$ -naphthylamine, crotonaldehyde, benzoic acid and coloring matter can be reacted and the product powdered for molding. Condensation products of this type are also applied in the utilization of waste rubber. A molding material is produced by mixing rubber waste or dust with a binding agent, consisting of an aldehyde-amine condensation product, which softens within the temperature range at which the rubber becomes soft or plastic.<sup>71</sup> Paraformaldehyde-amine condensation products are also utilized as adhesives, layers of material being bonded by the resin, which is then hardened by heating to 150°C. for 30 seconds.<sup>72</sup> Layers of a fibrous substance (paper, fabric) are processed in this manner to give laminated material for electrical insulation.<sup>73</sup> Haller and Kappeler<sup>74</sup> carried out the condensation below 100°C. between an aromatic amine (aniline, toluidine) and formaldehyde in the presence of hydrochloric acid, acetic acid or potassium bisulphate. The orange-red product is washed and then treated with alkali (a solution of sodium hydroxide, ammonia, milk of lime, sodium carbonate or alkali sulphide). A whitish mass resembling bone or horn is precipitated. Alternatively, the base and formaldehyde may be condensed first in an alkaline medium, and the product condensed with more formaldehyde in an acid medium, followed by washing and treatment with alkali. Fillers, softeners and pigments may be added. This process was further modified by treating the amine-aldehyde condensation product with an organic base, a neutral or acid salt or an organic acid (e.g., with methylamine, pyridine, aqueous ammonium chloride or acetic acid).<sup>75</sup> The aldehyde-amine reaction is continued until a jelly forms; then the supplemental amine, for example, is added, and the mass washed and dried.<sup>76</sup> The products have a wood-like, bony or horny appearance and are used as substitutes for bone and horn or as insulating materials. The product is further improved by adding salts soluble in water or alcohol to the amine. Thus, sodium chloride, ammonium chloride or ammonium nitrate is added to the aniline, hydrochloric acid and water before adding the formaldehyde.<sup>77</sup>

Acid solutions of the condensation products of aromatic amines and aldehydes in the form of gels and containing fillers (sawdust or mica) are pulverized during formation and the acid is separated.<sup>78</sup> After washing and drying, the material may

British P. 387,045, 1933, to Int. Gen. Electric Co., Inc.; *Chem. Abs.*, 1933, 27, 4701. British P. 388,030, 1933; *Chem. Abs.*, 1933, 27, 4701.

<sup>69</sup> Allgem. Elekt.-Ges., British P. 388,451, 1923, to Int. Gen. Electric Co., Inc.; *Chem. Abs.*, 1933, 27, 4701.

<sup>70</sup> Allgem. Elekt.-Ges., British P. 395,880, 1933, to Int. Gen. Electric Co., Inc.; *Chem. Abs.*, 1934, 28, 919. See also French P. 740,556, 1932, to Allgem. Elekt.-Ges.; *Chem. Abs.*, 1933, 27, 2831.

<sup>71</sup> Allgem. Elekt.-Ges., British P. 381,587, 1931, to Int. Gen. Electric Co., Inc.; *Brit. Chem. Abs.* B, 1933, 33. French P. 718,778, 1931, to Allgem. Elekt.-Ges.; *Chem. Abs.*, 1932, 26, 8406. See also H. Burmeister, U. S. P. 1,989,543, Jan. 29, 1935, to General Elec. Co.; *Chem. Abs.*, 1935, 29, 1906. German P. 598,943, 1934, to Allgem. Elekt.-Ges.; *Chem. Abs.*, 1934, 28, 7443.

<sup>72</sup> Allgem. Elekt.-Ges., British P. 316,194, 1928, to Int. Gen. Electric Co.; *Chem. Abs.*, 1930, 24, 1712. <sup>73</sup> Allgem. Elekt.-Ges., British P. 395,507, 1933, to Int. Gen. Electric Co., Inc.; *Chem. Abs.*, 1934, 28, 236.

<sup>74</sup> P. Haller and H. Kappeler, British P. 266,358, 1926; *Chem. Abs.*, 1928, 22, 691. A bubble-free resin is obtained by the acid condensation of an amine and formaldehyde. See British P. 390,000, 1932, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs.* B, 1933, 436.

<sup>75</sup> P. Haller and H. Kappeler, British P. 274,501, 1926; *Chem. Abs.*, 1928, 22, 2282. Swiss P. 127,950, 1926; *Chem. Abs.*, 1929, 23, 2256. Swiss P. 132,811, 1928; *Chem. Abs.*, 1930, 24, 476. British P. 306,972, 1928; *Chem. Abs.*, 1929, 23, 5339. Canadian P. 282,036, 1928; *Chem. Abs.*, 1928, 22, 3498. German P. 487,654, 1927; *Chem. Abs.*, 1930, 24, 1946.

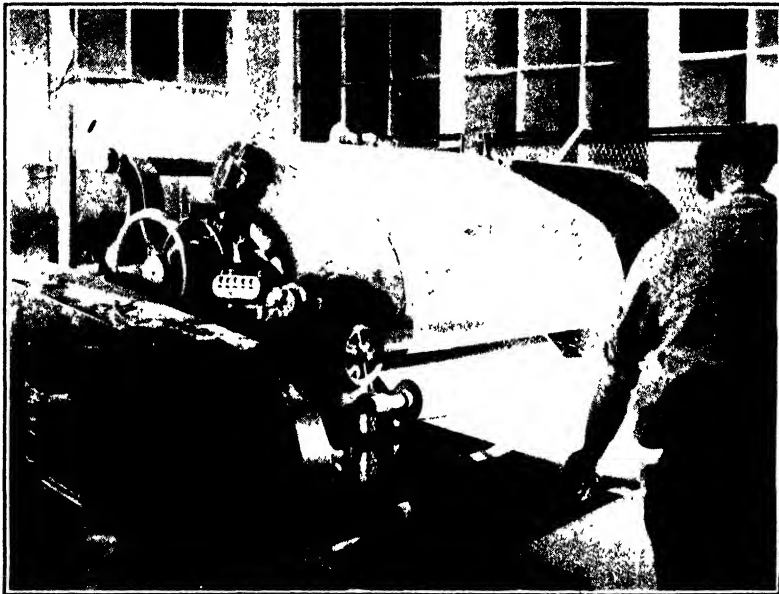
<sup>76</sup> P. Haller and H. Kappeler, U. S. P. 1,939,691, Dec. 19, 1933, to Ciba Products Corp.; *Chem. Abs.*, 1934, 28, 1560.

<sup>77</sup> P. Haller and H. Kappeler, German P. 496,981, 1929; *Chem. Abs.*, 1930, 24, 3615.

<sup>78</sup> French P. 753,146, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 1484. German P. 594,926, 1934; *Chem. Abs.*, 1934, 28, 4548.



be compressed into desired shapes. Molding powders, also, may be prepared from a mixture of a filling material and an acid solution of an aromatic amine and an aldehyde, which has a tendency to gelatinize. This is accomplished by disintegrating the gel during or after its formation but before solidification.<sup>79</sup> Thus, a solution of aniline hydrochloride in water is treated with formaldehyde and wood flour stirred in; the product is neutralized with sodium hydroxide, washed and dried. Amine-aldehyde resins have some use as coatings. A resin of low softening temperature with or without an added filling (quartz, kaolin) or softening material is selected and sprayed on the article to be coated.<sup>80</sup> By dissolving aniline-



*Courtesy Modern Plastics*

FIG. 116.—The machine illustrated cuts rolls of resin-impregnated paper into sheets for the production of laminated materials.

formaldehyde condensation products in a chlorohydrin (glycolchlorohydrin or glyceroldichlorohydrin), Gams and Frey<sup>81</sup> obtained a solution of use in varnishes and lacquers.

Amine-aldehyde reaction products give useful resins with phenols. Achtmeyer<sup>82</sup> produced non-inflammable friction compositions by the interaction of phenolic bodies with methylenediphenyldiamine,  $\text{CH}_2(\text{NHC}_6\text{H}_5)_2$ . This compound is prepared by allowing aniline, formaldehyde and potassium hydroxide to react in alcoholic solution at  $100^\circ\text{C}$ .<sup>83</sup> Specifically, the phenol friction-material is obtained by adding 100 parts of phenol to 75-100 parts of methylenediphenyldiamine in a steam-jacketed, open vessel provided with a stirrer. The mass is heated to boiling and heated further to remove water. This is treated with paraformaldehyde (7 to 10 per cent) and given a further heat treatment in order to convert the

<sup>79</sup> British P. 401,965, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 2860.

<sup>80</sup> Allgem. Elekt.-Ges., British P. 398,070, to Int. Gen. Electric Co., Inc.; *Chem. Abs.*, 1934, 28, 1557.

<sup>81</sup> A. Gams and K. Frey, U. S. P. 1,969,744, Aug. 14, 1934, to Ciba Products Corp.; *Chem. Abs.*, 1934, 28, 6330.

<sup>82</sup> W. Achtmeyer, U. S. P. 1,429,267, Sept. 19, 1922; *Chem. Abs.*, 1922, 16, 4023. Canadian P. 237,679, 1924; *Chem. Abs.*, 1924, 18, 1037.

<sup>83</sup> C. Eberhardt and A. Welter, *Ber.*, 1894, 27, 1804; *J.C.S.*, 1894, 66 (1), 451.

thin liquid product into a hard and insoluble resin. Dissolved in a high-boiling solvent (amyl acetate) before the final heat treatment, it may be used to impregnate porous and cellular materials. These compositions are baked at 300-400°C. and may be used as brake linings.

Bender<sup>88</sup> prepared a fusible, potentially reactive resin by reacting anhydroformaldehydeaniline with phenol. A fusible resin, soluble in organic solvents, was developed by Seebach<sup>84</sup> from a phenol, formaldehyde and aniline, toluidine or  $\alpha$ - or  $\beta$ -naphthylamine. More than 0.5 mol of phenol is used per mol of amine. Salts or derivatives (including, e.g., anthranilic acid, 1-naphthylamine-5-sulphonic acid) of amines are also employed in the process. The resins formed are characterized by containing a constant proportion of nitrogen.

Wayne<sup>85</sup> resolved petroleum emulsions by treating with a water-soluble condensation product such as that formed from sulphonated aniline and formaldehyde. Amine-formaldehyde resins were used by Siedler and Moeller<sup>86</sup> to prevent premature crystallization of supersaturated solutions of thiocarbanilide.

Burke<sup>87</sup> has used the reaction between amines and aldehydes to purify aldehyde-contaminated lower aliphatic alcohols. For example aniline was added to ethyl alcohol containing an aldehyde. The reaction product of amine and aldehyde was separated from the alcohol by distillation.

#### CONDENSATION OF OTHER AMINES WITH FORMALDEHYDE

Reaction between an amine (o-toluidine, aniline,  $\alpha$ - or  $\beta$ -naphthylamine) and at least one molecular proportion of formaldehyde may be brought about in the presence of water-soluble organic solvents for the amine, volatile by-products being distilled off *in vacuo* from the reaction product.<sup>88</sup> The reaction is carried out at 30-80°C. The resin from o-toluidine solidifies to a colophony-like mass, and has a softening point of 60°C. The addition of a salt of the amine or a further amount of the aldehyde increases the softening point. A bright yellow resin, softening at 80-85°C., is produced by heating 100 parts of o-toluidine and 70 parts of 94 per cent alcohol to boiling and adding 115 parts of formaldehyde with 0.4 part of formic acid.<sup>89</sup> Chlorotoluidines (1 mol) in alcohol (90 per cent) and 30 per cent formaldehyde (1.4 mols) gave a resin softening at 30°C., while  $\alpha$ -naphthylamine (1 mol) and formaldehyde (1.15 mols) gave one melting at 125°C. The yield of resin was improved, and its softening point was raised, on adding up to 10 per cent of a salt of the amine to the free amine employed. These resins are resistant to alkali, and may be used as resists in batik dyeing and printing.<sup>90</sup> They can be removed from the fabric by organic solvents, by weak acids or by treatment with hot water. The resins form brittle, clear yellowish to brownish masses of conchoidal fracture, which are soluble in many of the usual organic resin solvents. Solutions of the resins yield clear films (on glass, porcelain or metal) which are reported to be air-proof and, in some instances, light-proof.

On allowing the molten resin from naphthylamine residues to fall into a 40 per

<sup>88</sup> H. L. Bender, U. S. P. 1,955,731, Apr. 24, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 4256. These resins in which anhydroformaldehydeaniline is used to react with phenol simply for the methylene groups it contains are described in Chapter 20.

<sup>84</sup> F. Seebach, U. S. P. 1,683,701, Sept. 11, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1928, 22, 4262.

<sup>85</sup> T. B. Wayne, U. S. P. 1,912,330, May 30, 1933; *Chem. Abs.*, 1933, 27, 4066.

<sup>86</sup> P. Siedler and A. Moeller, U. S. P. 1,780,634, Nov. 4, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1931, 667.

<sup>87</sup> J. P. Burke, U. S. P. 1,987,601, Jan. 15, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 1931.

<sup>89</sup> W. Hildebrand, U. S. P. 1,777,140, Sept. 30, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 6042. French P. 693,750, 1930; *Chem. Abs.*, 1931, 25, 1645. German P. 452,009, 1927; *Chem. Abs.*, 1928, 22, 4262. British P. 274,155, 1926; *Chem. Abs.*, 1928, 22, 2072.

<sup>90</sup> W. Hildebrand, German P. 472,824, 1926; *Chem. Abs.*, 1929, 23, 3114.

<sup>91</sup> British P. 274,155, 1926, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1927, 756.

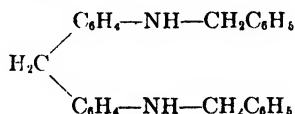
cent solution of formaldehyde containing 37 per cent of hydrochloric acid, and then heating for a short time to 300°C., an odorless resin with a softening point of 120°C. is obtained.<sup>91</sup> A novel application of amino resins, namely, in photography, is due to Beebe, Murray and Herlinger.<sup>92</sup> The following example illustrates the process: 35 g. of dimethylaniline, 14 g. of benzaldehyde and 4 g. of iodine are mixed and allowed to stand at room temperature for about 3 days. The result is a viscous green product. Through the addition of 1 g. of iodoform to 10 g. of the resin, a light-sensitive coating is produced which gives a print in about two minutes by optical projection in the usual manner. Benzylaniline, formaldehyde, water and a trace of concentrated hydrochloric acid likewise give a condensation product. When this is dissolved in benzene and iodoform added, the solution will give a light-sensitive film yielding a print in 30 seconds. The print may be developed with benzene and turpentine. The principal feature of this process is that the synthetic resin is capable of being condensed under the action of light, the iodine or organic iodine compound serving as a sensitizer. The condensed form of the resin is less soluble than the starting material, which introduces the possibility of obtaining a graded photographic image.<sup>93</sup>

As a substitute for copal and for resins used in sealing wax, Goldschmidt<sup>94</sup> proposed the employment of a resin formed by heating methylaniline or methyl-diphenylamine with formaldehyde and hydrochloric acid for 2 hours and then oxidizing.

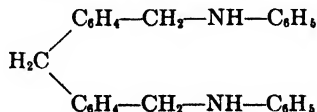
At an earlier date, Goldschmidt<sup>95</sup> reported the formation of an unstable product of high molecular weight in the reaction between asparagine,  $\text{COOH}-\text{CH}(\text{NH}_2)-\text{CH}_2-\text{CO}-\text{NH}_2$ , and formaldehyde.

#### BENZYLANILINE RESIN

Goldschmidt's investigation led Herzog<sup>96</sup> to experiments on the condensation of secondary amines in which a benzyl group forms one component. A resin was obtained by heating for one hour (under reflux) 9 g. of benzylaniline, 10 g. aqueous formaldehyde (40 per cent), 20 cc. of water and 1 cc. of hydrochloric acid. A 94 per cent yield of a brittle, brownish yellow, transparent resin was the result. This product is probably a condensation of two mols of benzylaniline with one mol of formaldehyde to form dibenzyl-diaminodiphenylmethane,



and finally by rearrangement<sup>97</sup> yielding diphenyldiaminodibenzylmethane,



<sup>91</sup> A. Steindorff, German P. 378,067, 1922, to Farb. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 1063A.

<sup>92</sup> M. C. Beebe, A. Murray and H. V. Herlinger, U. S. P. 1,587,272, June 1, 1926, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1926, 20, 2292. See also Chapter 24.

<sup>93</sup> See also British P. 269,806, 1926, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1928, 22, 1289. Swiss P. 126,216 and 126,217, 1926; *Chem. Abs.*, 1929, 23, 572.

<sup>94</sup> C. Goldschmidt, *Chem. Ztg.*, 1905, 29, 33; *J.S.C.I.*, 1905, 24, 552.

<sup>95</sup> C. Goldschmidt, *Chem. Ztg.*, 1893, 22, 374.

<sup>96</sup> W. Herzog, *Oester. Chem.-Ztg.*, 1921, 24, 16; *Chem. Abs.*, 1921, 15, 1410.

<sup>97</sup> Note German P. 58,072, 1890, to Farb. vorm. Meister, Lucius & Brünig; *Chem. Zentr.*, 1891, 2, 888.

The resin is easily soluble in benzene and trichloroethylene in the cold, and dissolves in turpentine on heating. When the resin is prepared in alcohol as a diluting medium, the product exhibits a redder tone. Neither organic acids nor alkalis act as resinifying agents. The product differs from the resin obtained by Goldschmidt in that the reaction proceeds only to the formation of diphenylmethane derivatives, which according to Herzog furnish a stable resin of use in the varnish industry, while Goldschmidt's resin from methylaniline and methyl-diphenylamine is a more complex product said to be subject to partial oxidation on exposure to air with the formation of strongly colored substances. Hence Herzog regarded Goldschmidt's resin as useful only for sealing wax.

#### NAPHTHYLAMINE RESINS

Acetaldehyde reacts with  $\beta$ -naphthylamine and with mixtures of  $\alpha$ - and  $\beta$ -naphthylamine in the presence of solvents, e.g., benzene, to form a hard resinous compound and a product resembling Canada balsam, respectively. These products have been proposed for use in the manufacture of varnishes and tracing paper. A product resembling rosin can be prepared by treating a mixture of equal parts of  $\alpha$ - and  $\beta$ -naphthylamine with formaldehyde; the mixture is agitated at 100°C., and, after cooling and separating the aqueous layer, the material is purified by kneading under hot water and is dried at about 120°C. A mixture of  $\alpha$ -naphthylamine and xylydine may also be used.<sup>18</sup>

Aniline, toluidine, xylydine or naphthylamine, alone or mixed, are condensed with acetaldehyde, aldol or crotonaldehyde (or mixtures of these compounds) by heating at 80-100°C. in a varnish solvent with the addition of a small amount of a condensing agent such as oxalic acid.<sup>19</sup> Benzene and its homologues, solvent naphtha or tetrahydronaphthalene are the usual solvents. Varnishes are obtained which dry quickly and yield a bright surface, stable to water and alkali. Soluble dye-stuffs may be added and also linseed oil or copal. As an example of the preparation of this type of varnish,  $\alpha$ -naphthylamine is dissolved in xylene, oxalic acid is added and the mixture is treated at 80°C. with a xylene solution of acetaldehyde. Caustic soda is then added, and the sodium oxalate which forms dissolves in the water produced in the reaction and is removed. The odor of the varnish is pleasant and bears no resemblance to that of  $\alpha$ -naphthylamine. A mixture of acetaldehyde, aldol and crotonaldehyde may be condensed in boiling solvent naphtha with  $\alpha$ -naphthylamine and aniline, in the presence of concentrated hydrochloric acid, and the acid removed with caustic soda or ammonia. When the solution is treated with naphtha-soluble black and diluted further with the solvent a deep black, rapid-drying varnish with a high luster is obtained.

Manfred, in a process for the manufacture of horn-like masses with elastic properties, used an albuminous material with, among other possibilities, an aldehyde-amine condensation product.<sup>20</sup> N-Methyl-p-aminophenols are prepared by reducing the condensation product of the corresponding p-aminophenol and formaldehyde with activated aluminum in alkaline solution. Reduction and condensation may be effected in a single operation.<sup>201</sup> Böhler<sup>202</sup> found that mixtures of phenol-formaldehyde or resinitannol-formaldehyde and amine-formaldehyde resins, prepared either by fusing the components together or by using a common solvent,

<sup>18</sup> German P. 300,685 and 303,953, 1917, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1922, 41, 382A.

<sup>19</sup> K. Daimler, German P. 372,855, 1920, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 1040A.

<sup>20</sup> O. Manfred, British P. 281,223, 1927; *Brit. Chem. Abs. B*, 1928, 829.

<sup>201</sup> British P. 306,939, 1923, to Chem. Fabr. Grünau Landshoff & Meyer A.-G.; *Chem. Abs.*, 1929, 23, 519B.

<sup>202</sup> C. Böhler, German P. 545,270, 1929; *Chem. Abs.*, 1932, 26, 3126.

gave products which hardened less readily than the phenol or tannol resin alone, and could be used for making molded articles. A yellow resin, to which the name A.F.S. has been given, was prepared by the condensation of aniline, formaldehyde and sulphur. It appears to be serviceable as a substitute for Canada balsam in mounting microscopic objects, and is used in the same manner.<sup>108</sup>

#### RESINS FROM AMINES AND OTHER ALDEHYDES

To a certain extent the processes already described using formaldehyde for resin production may be applied without further modification so as to utilize other aldehydes. The present section is devoted, however, to the description of a number of reactions in which these higher aldehydes are mentioned specifically.

The condensation products prepared from a primary or a secondary amine (o-toluidine, m-xylydine or cresidine) with an aliphatic aldehyde (e.g., formaldehyde, acetaldehyde or crotonaldehyde) in the presence of hydrochloric acid are proposed mordanting agents for dyeing (with acid and chrome colors) vegetable fibers, viscose and cupranmonium silks. The formaldehyde-o-toluidine product, e.g., gives insoluble lakes with acid and chrome dyes. The mordant may be used on wool, silk, leather or furs, but not on cellulose acetate fabrics.<sup>104</sup>

Crotonaldehyde, condensed with amines such as aniline or  $\alpha$ -naphthylamine, in the absence of a condensing agent forms synthetic resins.<sup>105</sup> When aniline is gradually added to crotonaldehyde at a temperature below 50°C., the mixture being stirred for 3 hours and allowed to stand and finally heated *in vacuo* to 125°C., a brittle resin forms. The reactants may be dissolved in solvents (benzene, acetone or alcohol).<sup>106</sup>

A synthetic resin prepared from aniline and furfural was found by Moss and White<sup>107</sup> to be compatible with cellulose acetate. When added to lacquers containing the latter, clear solutions were formed, which, on drying, produced clear, hard, tough and firmly adherent films, brown in the undyed or unpigmented form. In the preparation of the resin, equimolecular proportions of furfural and aniline are heated under reflux for from 1 to 3 hours at 170°C. The brittle, black resin formed is soluble in acetone or benzene, the solution in acetone being miscible with cellulose acetate solutions in the usual solvents. These resins lighten in color on exposure to light, whereas phenol-formaldehyde resins darken. A mixture of the two resins is reported to give a light-fast film. The following is the composition of a mixture for producing such a film:

Cellulose acetate . . . . .	10 parts
Aniline-furfural resin . . . . .	5 "
Phenol-formaldehyde resin . . . . .	5 "
Acetone . . . . .	100 "

Natural resins, plasticizers and pigments may also be incorporated in these resins.

Acetaldehyde or furfural-amine resins may be used in impregnating a fibrous pulp, as already described in the case of formaldehyde-aniline resins.<sup>108</sup> Furfural may also be condensed with the fusible reaction product of an aromatic

<sup>108</sup> G. D. Hanna, *Science*, 1927, 65, 42, and *J. Roy. Microscopical Soc.*, 1931, 50, 424; *Chem. Abs.*, 1931, 25, 1858. See also H. G. Fisk, *Amer. J. Sci.*, 1932, (5) 23, 172; *Brit. Chem. Abs. A*, 1932, 247.

<sup>104</sup> J. P. Sisley, French P. 713,283, 1930, to Soc. anon. des matières colorantes et produits chim. de Saint-Denis; *Chem. Abs.*, 1932, 26, 1800. See also *Rev. gén. Mat. Col.*, 1932, 36, 334, *Brit. Chem. Abs. B*, 1932, 978.

<sup>105</sup> W. Kropp, U. S. P. 1,640,899, Aug. 30, 1927; *Chem. Abs.*, 1927, 21, 3474.

<sup>106</sup> British P. 270,433, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 1696.

<sup>107</sup> W. H. Moss and B. B. White, U. S. P. 1,902,255, March 21, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 3350. W. H. Moss, U. S. P. 1,902,256 and 1,902,257, March 21, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 3350.

<sup>108</sup> R. H. Kienle and W. J. Scheiber, British P. 352,140, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1932, 26, 4144.

amine and formaldehyde (formed with not more than 0.2 mol of acid per mol of amine), a filler may be added and the product hardened by hot compression.<sup>100</sup> Cinnamaldehyde and aniline yield a synthetic resin.<sup>100</sup> Aromatic amines have also been reported as reacting with  $\alpha,\beta$ -disubstituted acraldehydes forming condensation products.<sup>101</sup> Cherry and Kurath<sup>102</sup> found that a condensation would take place between amines, organic acids and aldehydes, forming wax substitutes and plasticizing agents. The aldehydes used include formaldehyde and furfural. Appropriate acids are stearic, succinic, benzoic and oleic, and also rosin. Aniline, toluidine or naphthylamine represent types of amines which may be employed. As an example, 30 parts of rosin are heated to 170-200°C. with 10 parts of aniline for 3 hours. Nine parts of furfural are added and the heating continued at 200°C. for half an hour. The product is not as brittle as rosin, and has a plasticizing effect on phenolic molding compositions.<sup>103</sup> When half of the rosin is replaced by stearic acid, a substance with both wax-like and resinous characteristics results. Shepard<sup>104</sup> found that products such as those formed in the condensation between acetaldehyde and aniline may be freed from water by melting with about 10 per cent of a fatty acid (stearic acid) and heating to evaporate the water.

Huxham<sup>105</sup> added 90 parts of a furfural-aniline resin to 100 parts of a fusible phenol-aldehyde condensation product dissolved in a high-boiling hydrocarbon solvent. The mixture is hardened at 150°C. for several hours and may be used as a cold-molding composition for the manufacture of insulators. Powell<sup>106</sup> has made use of the synthetic resins from amines and aldehydes for preventing the rancidification of soap. Thus, 0.02 to 0.5 per cent of the product from aniline and acetaldehyde was sufficient. It is possible to add the amine to the raw oil or fats prior to their saponification, and to add the aldehyde to the saponified product, the two substances reacting while incorporated in the soap.

A mixture of dimethylquinol and aniline on standing for a long period yields an oil which, on distillation, gives a soft resin.<sup>107</sup> Carnahan and Hurd<sup>108</sup> obtained a yellow resinous solid melting at 76°C. by holding a mixture of acrolein and aniline at 10°C. On heating this mass it changed into higher-melting resins.

#### MISCELLANEOUS PRODUCTS FROM AMINES

Daniels and Snell<sup>109</sup> have used diphenylguanidine and triphenylguanidine for hardening shellac. The following example illustrates the method of working. A mixture of shellac (50 lb.), denatured alcohol (15 gallons), triphenylguanidine (0.5 lb.) and wood flour (300 lb.) is thoroughly dispersed, and the alcohol then removed. Hot molding of the powdery product gives a finished article which is resistant to alcohol, and remains hard at temperatures considerably above the softening point of natural shellac. Other agents which produce the same effect are aldehyde-ammonia, an aminonaphthalene, a secondary aromatic amine, a

<sup>100</sup> British P. 404,469, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs.* B, 1934, 244.

<sup>101</sup> French P. 35,202, 1928, addn. to 644,075, to La fibre Diamond; *Chem. Abs.*, 1930, 24, 2317.

<sup>102</sup> British P. 264,674, 1926, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1927, 230.

<sup>103</sup> O. A. Cherry and F. Kurath, U. S. P. 1,800,815, April 14, 1931, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1931, 25, 3503.

<sup>104</sup> O. A. Cherry and F. Kurath, U. S. P. 1,894,580, Jan. 17, 1933, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1933, 27, 2592.

<sup>105</sup> M. G. Shepard, British P. 276,627, 1926; *Chem. Abs.*, 1928, 22, 2475.

<sup>106</sup> T. S. Huxham, U. S. P. 1,606,943, Nov. 16, 1926, to American Insulator Corp.; *Brit. Chem. Abs.* B, 1927, 85.

<sup>107</sup> J. R. Powell, U. S. P. 1,673,657, June 5, 1928, to Armour & Co.; *Chem. Abs.*, 1928, 22, 2677.

<sup>108</sup> E. Bamberger, *Ber.*, 1927, 60, 977; *Chem. Abs.*, 1927, 21, 2124.

<sup>109</sup> F. L. Carnahan and C. D. Hurd, *J.A.C.S.*, 1930, 52, 4590.

<sup>110</sup> E. A. Daniels and H. S. Snell, U. S. P. 1,673,803 to 1,673,808, June 19, 1928, to Western Electric Co.; *Chem. Abs.*, 1928, 22, 2550.

piperidine-carbon disulphide addition product, and sodium  $\beta$ -naphthoxide. The condensation product of aldol and diphenylguanidine is used by Chamberlain<sup>120</sup> to retard the action of the acid in a pickling bath on the metal itself, without interfering with the removal of scale or oxide. The products from formaldehyde, acetaldehyde or heptaldehyde and aniline, and those from furfural and diethylamine or diphenylguanidine may be used for the same purpose.

Polymerization products of amides or imides with an aldehyde find use as bonding agents for abrasives on paper and other materials.<sup>121</sup> A molding composition for the production of insulators may be made by combining coal residues with aromatic amines.<sup>122</sup> Resins have also been obtained from amines, aldehydes and drying oils. Thus a viscous oil is formed from tung oil, phenylamine and phenylamine hydrochloride. This oil is heated with anhydroformaldehyde/aniline for 1-2 hours at 200°C. and then treated with formaldehyde to give the final product.<sup>123</sup>

### ACETYLENE CONDENSATIONS

Acetaldehyde, prepared by passing acetylene at 25 pounds per square inch into 25-35 per cent sulphuric acid containing mercurous sulphate at 68-80°C., may be removed from the gaseous reaction product by combination with a primary amine (e.g., aniline, toluidines or xylidines). Absorption takes place in a series of four scrubbing towers, each followed by a condenser and trap for removal of water formed. The acetylene escaping from the final tower is scrubbed and returned to the circuit.<sup>124</sup>

Resin-like condensation products are formed on treating primary aromatic amines with acetylene in the presence of a catalyst (a mercury compound) and in the absence of water or alcohol. Thus, aniline treated with acetylene in the presence of mercuric chloride gave a red resin, which melted at 70-104°C.<sup>125</sup> These products are applied as lacquers or alkali-resistant varnishes and, in the rubber industry, as vulcanization accelerators and anti-oxidants; they may also be converted into new products by sulphonation, nitration, reduction or by treatment with aldehydes. As an example of the method, 280 parts of aniline are stirred into 27 parts of mercuric chloride in an atmosphere of acetylene at 30-50°C., until no more of the gas is absorbed. The product is dissolved in mineral acid, and the mercury deposit is filtered off. A reddish resin remains after removing unchanged aniline by steam distillation.

When acetylene and aniline vapors are passed over alumina at 360-420°C., lepidine is formed. The same product can be obtained from acetaldehyde and aniline at 400-500°C.<sup>125a</sup> Matheson<sup>126</sup> conducted acetylene into aniline at 90°C. in the presence of cuprous chloride as a catalytic material, and found that the substances combined in approximately equimolecular proportions. On fractionally distilling the product, the fraction boiling at 200-275°C. having a formula believed to

<sup>120</sup> G. D. Chamberlain, U. S. P. 1,719,649, July 2, 1929, to R. T. Vanderbilt Co.; *Chem. Abs.*, 1929, 23, 3895.

<sup>121</sup> French P. 756,564, 1933, to Minnesota Mining and Mfg. Co.; *Chem. Abs.*, 1934, 28, 2490.

<sup>122</sup> French P. 764,338, 1934, to Studien- & Verwertung-G.m.b.H.; *Chem. Abs.*, 1934, 28, 5612.

<sup>123</sup> French P. 770,400, 1934, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1935, 29, 524.

<sup>124</sup> C. N. Hand, British P. 269,556, 1927, to Rubber Service Lab. Co.; *Brit. Chem. Abs. B.*, 1928, 82.

<sup>125</sup> German P. 525,905, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1931, 25, 4726.

French P. 655,583, 1928; *Chem. Abs.*, 1929, 23, 4090. Swiss P. 129,592, 1927; *Chem. Abs.*, 1929, 23, 3549. British P. 292,168, 1927; *Chem. Abs.*, 1929, 23, 1518. Swiss P. 131,274 to 131,276, 1927, addns. to 129,592, 1927; *Chem. Abs.*, 1929, 23, 3822. See also P. Schetelig and T. Sutter, U. S. P. 1,893,249, Jan. 3, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1933, 27, 2319.

<sup>125a</sup> A. E. Chichibabin and M. P. Oparina, *Ber.*, 1927, 60, 1873; *Chem. Abs.*, 1928, 22, 83.

<sup>126</sup> H. W. Matheson, U. S. P. 1,788,773, Jan. 13, 1931, to Canadian Electro Products Co.; *Chem. Abs.*, 1931, 25, 1120. Quinaldine and its homologues, substituted products and polymers are formed in this reaction. See British P. 296,423, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 14, 441; *Brit. Chem. Abs. B.*, 1929, 747.

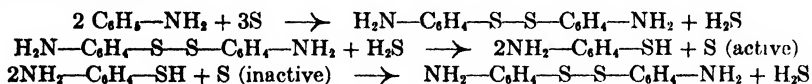
be  $C_6H_5-NH-CH=CH_2$ , was isolated and allowed to react with acetaldehyde. The product had good qualities as a rubber vulcanization accelerator.

Rötger and Schlecht<sup>127</sup> obtained a tar-like mass by heating acetylene, aniline vapor and steam to 350°C. in contact with a catalyst obtained by soaking silica gel in zinc nitrate and heating. Silica gel is an efficient catalyst for the alkylation of aniline, but is fouled by the polymerization products resulting from the combination of acetaldehyde (formed in the above reaction) and aniline.<sup>128</sup> The reaction between acetylene and aniline at higher temperatures (e.g., 700°C.) with a catalyst (e.g., nickel, silica or platinum) gave indole.<sup>129</sup>

#### AMINE-ALDEHYDE CONDENSATION PRODUCTS AS VULCANIZATION ACCELERATORS

Bysov<sup>130</sup> stated that any substance soluble in rubber and capable of dissolving sulphur would function, by aiding the distribution of sulphur, as a vulcanization accelerator, and that any substance soluble in rubber and able to form a precipitate insoluble in rubber would serve in a like manner.

The role of aniline as an accelerator of rubber vulcanization was studied by Kimishima<sup>131</sup> who found that, at the temperature of hot vulcanization, aniline reacts with sulphur giving hydrogen sulphide, dithioaniline and a small quantity of thioaniline and resinous materials. In an atmosphere of hydrogen sulphide, dithioaniline acts as a powerful accelerator. The mechanism of the accelerating effect is given as follows:



Investigators in the rubber industry have found that many amine-aldehyde condensation products are satisfactory as vulcanization accelerators.<sup>132</sup> Representatives of the following combinations have been prepared and are mentioned later in this chapter: primary aromatic amines with saturated aliphatic aldehydes, primary aromatic amines with aromatic aldehydes, primary aromatic amines with unsaturated aliphatic aldehydes, primary aliphatic amines with aliphatic aldehydes and ammonia with unsaturated aldehydes. Also, secondary amines and urea have been employed. Several investigators have used acid condensing agents. The proportions of aldehyde to amine have been varied and the initial reaction products have been combined with further amounts of aldehyde. Finally, the preparation of vulcanization accelerators has been varied by combining carbon disulphide or various mercaptothiazoles with the amine-aldehyde condensation products.

An example of the use of these amine-aldehyde condensation products is the semi-vulcanized gasket formed by incorporating with rubber the reaction product of an aliphatic aldehyde (3 mols) and a primary aromatic amine (2 mols) as described by Smith and Schreiner.<sup>133</sup> Rubber to be used in the manufacture of various other products is combined with fragments, softening at 80-150°C., formed from colophony and aldehyde-aniline accelerators.<sup>134</sup>

<sup>127</sup> H. Rötger and L. Schlecht, German P. 527,960, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 5259.

<sup>128</sup> A. B. Brown and E. E. Reid, *J.A.C.S.*, 1924, 46, 1836.

<sup>129</sup> R. Majima, T. Unno and K. Ono, *Ber.*, 1922, 55, 3354; *Chem. Abs.*, 1923, 17, 1016.

<sup>130</sup> H. Bysov, *India Rubber J.*, 1923, 70, 859; *Chem. Abs.*, 1926, 20, 313.

<sup>131</sup> T. Kimishima, *J. Chem. Ind. Japan*, 1922, 25, 1141; *Chem. Abs.*, 1923, 17, 3626.

<sup>132</sup> See M. Farberov and A. Korunova, *J. Rubber Ind., U. S. S. R.*, 1934, 10 (1), 25; *Brit. Chem. Abs.*, 1934, 597.

<sup>133</sup> A. H. Smith and C. L. Schreiner, U. S. P. 1,881,142, Oct. 4, 1932, to Rubber Service Lab. Co.; *Chem. Abs.*, 1933, 28, 631.

<sup>134</sup> D. F. Twiss, British P. 293,502, 1927, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs.*, 1928, 681.



Cadwell<sup>135</sup> condensed aniline and acetaldehyde in a water medium having a hydrogen ion concentration between  $1 \times 10^{-3}$  and  $2.5 \times 10^{-6}$  to produce a rubber vulcanization accelerator. A higher acid content lessens the accelerating proficiency, and too little acid decreases the yield of the product. The reaction temperature used is 135-140°C.<sup>136</sup> and other starting materials include: heptaldehyde and aniline, heptaldehyde and ammonia, butyraldehyde and aniline, aldol and aniline, nonaldehyde and aniline and heptaldehyde with ethylamine, p-toluidine, benzidine, p-phenylenediamine, p-aminodimethylaniline or urea.<sup>137</sup> Halogen derivatives of the condensation products are also employed.<sup>138</sup> In the condensation, aldehydes with a chain of carbon atoms (i.e., higher than formaldehyde) are preferred.<sup>139</sup> The reaction between 2 mols of an aldehyde (formaldehyde, acetaldehyde, benzaldehyde), 2 mols of a primary amine (aniline, ethylamine, isopropylamine, hydroxyethylamine) and 1 or 2 mols of carbon disulphide was shown by Powers<sup>140</sup> to give accelerators. Similar products result when an aldehyde is treated with a substituted ammonium salt of a mono-substituted dithiocarbamic acid. Sebrell<sup>140a</sup> accelerated vulcanization by employing an acetal-dol-aniline reaction product. Mercaptonaphthothiazoles and mercaptomethylthiazoles combined with the reaction products of various aldehydes and primary amines perform a similar function,<sup>140b</sup> for the resulting resinous compounds are easily dispersed in rubber. The reaction product of 2-mercaptobenzothiazole (2 mols) with 2,4-diaminodiphenylamine (1 mol) condenses with acetaldehyde (1 mol), crotonaldehyde (1 mol), butyraldehyde and heptaldehyde yielding accelerating compositions.<sup>141</sup> Using aldehydes, having a hydroxyl group substituted in an aromatic nucleus, and amines, Teppema<sup>142</sup> obtained rubber accelerators that also improved the quality of the final product. Thus, 1 mol of  $\beta$ -hydroxynaphthaldehyde is refluxed for several hours with aniline. A yellow crystalline compound is obtained which on heating evolves an oil and leaves a resinous mass. This resin has accelerating properties not possessed by the yellow crystalline compound.

Scott<sup>143</sup> treated the amine-aldehyde reaction products with additional aldehyde to give accelerating substances. As an example, 1 mol of aniline is heated at 80°C. with 1.5 mols of acetaldehyde or a higher homologue, and 40 per cent formaldehyde is added to the resulting material. A slightly modified procedure involves heating the amine-aldehyde product with formaldehyde or acetaldehyde at 95°C. under increased pressure for 4 hours, and then under reduced pressure.<sup>144</sup> The amine-aldehyde may also be treated, below 30°C., with 2

<sup>135</sup> S. M. Cadwell, U. S. P. 1,627,230, May 3, 1927, to Naugatuck Chem. Co.; *Chem. Abs.*, 1927, 21, 2137. British P. 216,478, 1923; *J. S. C. I.*, 1924, 43, 848F.

<sup>136</sup> S. M. Cadwell and A. T. Maximoff, British P. 259,933, 1926, to Naugatuck Chem. Co.; *Brit. Chem. Abs. B*, 1927, 393.

<sup>137</sup> S. M. Cadwell, British P. 259,933, 1925; *Chem. Abs.*, 1927, 21, 3490.

<sup>138</sup> S. M. Cadwell, British P. 298,537, 1926, to Naugatuck Chem. Co.; *Chem. Abs.*, 1929, 22, 3376. British P. 279,815, 1926; *Chem. Abs.*, 1929, 22, 3065.

<sup>139</sup> S. M. Cadwell, British P. 302,176, 1927, to Naugatuck Chem. Co.; *Brit. Chem. Abs. B*, 1929, 495.

<sup>140</sup> D. H. Powers, U. S. P. 1,732,532, Oct. 22, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 23, 266. U. S. P. 1,975,588, Oct. 2, 1934; *Chem. Abs.*, 1934, 28, 7244. U. S. P. 1,993,803, Mar. 12, 1935. See also German P. 496,979, 1926, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 24, 3615. Dibenzylamine-formaldehyde condensation products are also treated with carbon disulphide by W. Scott (U. S. P. 1,727,391, Nov. 26, 1929, to Rubber Service Lab. Co.; *Brit. Chem. Abs. B*, 1930, 603) to give accelerators.

<sup>140a</sup> L. B. Sebrell, U. S. P. 1,754,865, April 15, 1930, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1930, 24, 2918.

<sup>140b</sup> L. B. Sebrell, British P. 297,051, 1927, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1929, 23, 2603. See also British P. 226,749 and 237,001, 1926, to Rubber Service Lab. Co.; *Brit. Chem. Abs. B*, 1928, 377.

<sup>141</sup> R. L. Sibley, German P. 568,266 and British P. 366,554, 1930, to Rubber Service Lab. Co.; *Chem. Abs.*, 1933, 27, 2063.

<sup>142</sup> J. Teppema, Canadian P. 288,103, 1929, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1929, 23, 1776. British P. 298,622, 1928; *Brit. Chem. Abs. B*, 1929, 652.

<sup>143</sup> W. Scott, U. S. P. 1,638,220, Aug. 9, 1927, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1927, 858. U. S. P. 1,571,739, Feb. 2, 1926; *Chem. Abs.*, 1926, 20, 1004.

<sup>144</sup> C. O. North, U. S. P. 1,639,957, Aug. 23, 1927, to Rubber Service Lab. Co.; *Chem. Abs.*, 1927,

per cent of concentrated hydrochloric acid, neutralized and then heated with formaldehyde or acetaldehyde.<sup>143</sup> Alternatively, the reaction can take place by heating at 100°C. and dehydrating at 105°C.<sup>144</sup> North<sup>147</sup> prepared similar products from aniline and acetaldehyde by subsequent reaction with additional acetaldehyde or other aliphatic aldehyde higher than formaldehyde. He also formed compounds from the reaction of carbon disulphide on these aldehyde derivatives of the Schiff's bases.<sup>148</sup> An accelerating composition was prepared by North<sup>149</sup> by combining the reaction product from 3 mols of butyraldehyde and 1 mol of aniline with the product from 3 mols of acetaldehyde and 2 mols of aniline in a mixture of creosote oil and pine oil. The product of the condensation of butyraldehyde and aniline, on evaporating off the water formed and heating at 100-145°C. for 2-20 hours, serves as an accelerating agent.<sup>150</sup> North and Christensen<sup>151</sup> employed crotonaldehyde and aniline as the basis for an accelerator.

In the process of Cambron,<sup>152</sup> aldehyde-amine accelerators are produced, without the use of excess aldehyde, by condensing the reagents without water in the presence of acidic substances (e.g., zinc chloride, hydrochloric or sulphuric acid, aluminum chloride, chlorodinitrobenzene). No solvent is used and the product can be finely ground without danger of subsequent lumping. An accelerating resin, from aniline and aliphatic aldehydes, known as "Vulcone," retards pre-vulcanization in rubber compositions and is said to improve the plasticity of the product.<sup>153</sup>

Unsaturated aldehydes also are employed in the preparation of vulcanization accelerators. Morton<sup>154</sup> used  $\alpha$ -ethyl- $\beta$ -methylacrolein with an amine (aniline), neutralized by abietic acid, in making a stable agent.  $\alpha,\beta$ -Dialkyl-substituted acroleins were also employed by Kropp<sup>155</sup> to react with aniline in the presence of an inert solvent (benzene) and a condensing agent (zinc chloride). The reaction product of an unsaturated aldehyde (crotonaldehyde) and an amine gives a vulcanizing accelerator.<sup>156</sup> Unsaturated aldehydes with conjugated double linkings and aromatic amines serve the same purpose.<sup>157</sup> Williams and Burnett<sup>158</sup> made

21, 3284. See also British P. 263,517, 1925, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B.* 1927, 150.

<sup>143</sup> W. Scott, U. S. P. 1,639,903, Aug. 23, 1927, to Rubber Service Lab. Co.; *Chem. Abs.*, 1927, 21, 3284.

<sup>144</sup> C. O. North, U. S. P. 1,659,151, Feb. 14, 1928, to Rubber Service Lab. Co.; *Reissue* 17,511, Dec. 3, 1929 (*Brit. Chem. Abs. B.* 1930, 69); *Brit. Chem. Abs. B.* 1928, 308. U. S. P. 1,659,152, Feb. 14, 1928; *Brit. Chem. Abs. B.* 1928, 301.

<sup>147</sup> C. O. North, U. S. P. 1,619,953, March 8, 1927; *Chem. Abs.*, 1927, 21, 1365; *Brit. Chem. Abs. B.* 1927, 392; *Reissue* 17,511, Dec. 3, 1929; *Chem. Abs.*, 1930, 24, 981. U. S. P. 1,467,984, Sept. 11, 1923, *J.S.C.I.*, 1923, 1083A. British P. 251,005, 1925, *Chem. Abs.*, 1927, 21, 1378.

<sup>149</sup> C. O. North, U. S. P. 1,732,770, Oct. 22, 1929, to Rubber Service Lab. Co.; *Chem. Abs.*, 1930, 24, 266.

<sup>150</sup> C. O. North, U. S. P. 1,787,258, Dec. 30, 1930, to Rubber Service Lab. Co.; *Chem. Abs.*, 1931, 25, 1119.

<sup>151</sup> C. O. North, U. S. P. 1,897,210, Feb. 14, 1933, to Rubber Service Lab. Co.; *Chem. Abs.*, 1933, 27, 2845.

<sup>152</sup> C. O. North and C. W. Christensen, U. S. P. 1,670,312, May 22, 1928, to Rubber Service Lab. Co.; *Brit. Chem. Abs. B.* 1928, 533.

<sup>153</sup> A. Cambron, U. S. P. 1,754,010, April 8, 1930, to Roessler & Hasslacher Chem. Co.; *Chem. Abs.*, 1930, 24, 2640. U. S. P. 1,858,577, May 17, 1932; *Chem. Abs.*, 1932, 26, 3960. C. S. Williams (U. S. P. 1,942,670, Jan. 16, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 2220) eliminated water from amine-aldehyde accelerators by adding calcium oxide.

<sup>154</sup> Société du Pont de Nemours. *Kunststoffe*, 1925, 15, 114. See also L. Stoll. *Gummi-Ztg.*, 1925, 40, 676; *Chem. Abs.*, 1926, 20, 843; and A. D. Lutringer, *Caoutchouc et Gutta-Percha*, 1925, 22, 12, 587; *Chem. Abs.*, 1925, 19, 1792.

<sup>155</sup> H. A. Morton, U. S. P. 1,784,703, Dec. 9, 1930; *Chem. Abs.*, 1931, 25, 438.

<sup>156</sup> W. Kropp, U. S. P. 1,584,849, Dec. 1, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1157. U. S. P. 1,845,755, Feb. 16, 1932; *Chem. Abs.*, 1932, 26, 2347. U. S. P. 1,616,378, Feb. 1, 1927; *Brit. Chem. Abs. B.* 1927, 305. German P. 545,692, 1925; *Chem. Abs.*, 1932, 26, 3690.

<sup>157</sup> L. B. Sobrell, U. S. P. 1,676,838, July 10, 1928, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1928, 22, 2318.

<sup>158</sup> C. O. North and C. W. Christensen, Canadian P. 258,626, 1925, to Rubber Service Lab. Co.; *Brit. Chem. Abs. B.* 1927, 393. See also British P. 264,673, 1926, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.* 1927, 230.

<sup>159</sup> I. Williams and W. B. Burnett, U. S. P. 1,780,326 and 1,780,334, Nov. 4, 1930, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B.* 1931, 667. British P. 249,113, 1925; *Chem. Abs.*, 1927, 21, 836. British P. 263,583, 1925; *Chem. Abs.*, 1928, 22, 186. See also German P. 478,948, 1926, to Grasselli Chemical Co.; *Chem. Abs.*, 1929, 23, 4713. The deterioration of amine-aldehyde compounds (e.g.,

various amine-aldehyde products for use in rubber vulcanization by allowing 2-20 mols of an aldehyde to react with an amino compound under conditions effecting the elimination of water.  $\alpha$ -Unsaturated aldehydes are excluded, and the condensation of n-butaldehyde with aniline or o-toluidine and heptaldehyde with n-butylamine is carried out in the presence of n-butyric, stearic, n-valeric, acetic or sulphuric acid. As the proportion of aldehyde in the product increases, the curing power rises to a maximum and then decreases. The condensation products of amines (aniline, butylamine or o-tolyl guanide) and saturated aldehydes (butyr-aldehyde, heptaldehyde or propionaldehyde) with, preferably, weak organic acids as condensing agents are unaffected by the presence of carbon black in the rubber mix.<sup>100</sup> Additional condensing agents used are oleic acid, salicylic acid, picric acid, hydrochloric acid, phosphoric acid, zinc chloride, amine salts and acid anhydrides or halides.

The amine-aldehyde products were treated with a higher fatty acid by Bridgwater and Slack<sup>100</sup> and then added to the rubber mix as accelerators. Thus, methylenediphenylimine, from aniline and formaldehyde at 70-80°C., is mixed with molten stearic acid and then incorporated in the rubber mix. Butylidenedianilide (from the reaction of 1 mol of butyraldehyde and 2 mols of aniline) or other alkylidenedianilines condense with heptaldehyde to form vulcanization accelerators.<sup>101</sup> The reaction product of heptaldehyde and aniline may also be combined with a halogen-substituted toluene derivative (e.g., benzotrichloride) in the preparation of accelerators.<sup>102</sup>

The condensation product of ammonia with an unsaturated aldehyde possesses accelerating properties.<sup>103</sup> Ammonia-aldehyde compounds, such as hexamethylenetetramine or crotonaldehydeammonia, and a mercaptobenzothiazole are treated with an aliphatic aldehyde (formaldehyde or aldol) to prepare accelerating substances.<sup>104</sup>

A secondary amine (dibenzylamine, 2 mols) reacts with an aldehyde (para-formaldehyde) and the product formed is treated while in ether solution with carbon disulphide.<sup>105</sup> Diethylamine with paraformaldehyde and piperidine with furfural may also be treated with carbon disulphide, and the resulting compositions find use as accelerators in the vulcanization of rubber with sulphur.<sup>106</sup>

Shepard and Adams<sup>107</sup> mixed a water solution of hexamethylenetetramine with ethyl chloride in an autoclave and heated the addition product to effect hydrolysis. The compound formed is triethyltrimethylenetriamine which may be separated by settling after the addition of sodium hydroxide, and it is used to accelerate vulcanization.

The reaction product of an amine and an aldehyde-bisulphite compound was condensed by Fritzsche<sup>108</sup> with an aldehyde forming vulcanization accelerators.

aniline-heptaldehyde) can be prevented by treatment with a polyhydroxy compound (S. I. Strickhouser, U. S. P. 1,805,194, May 12, 1931, to Naugatuck Chem. Co.; *Chem. Abs.*, 1931, 25, 3669. British P. 344,690, 1930; *Brit. Chem. Abs. B*, 1931, 631. French P. 692,635, 1930; *Chem. Abs.*, 1931, 25, 1537).

<sup>100</sup> W. B. Burnett and I. Williams, British P. 365,980 and 365,981, 1926; *Chem. Abs.*, 1928, 22, 512.  
<sup>101</sup> E. G. Bridgwater and A. S. Slack, U. S. P. 1,705,713, March 9, 1929, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1929, 652.

<sup>102</sup> C. O. North and W. Scott, U. S. P. 1,737,384, Nov. 26, 1929, to Rubber Service Lab. Co.; *Chem. Abs.*, 1930, 24, 752.

<sup>103</sup> O. Behrend, U. S. P. 1,896,535, Feb. 7, 1933, to Rubber Service Lab. Co.; *Chem. Abs.*, 1933, 27, 2845. U. S. P. 1,891,743, Dec. 20, 1932; *Chem. Abs.*, 1933, 27, 2063.

<sup>104</sup> British P. 333,174, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 959.

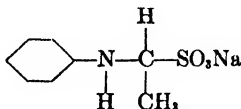
<sup>105</sup> W. Scott, U. S. P. 1,747,183, Feb. 18, 1930, to Rubber Service Lab. Co.; *Chem. Abs.*, 1930, 24, 1766.

<sup>106</sup> W. Scott, U. S. P. 1,737,391, Nov. 26, 1929, to Rubber Service Lab. Co.; *Chem. Abs.*, 1930, 24, 753.

<sup>107</sup> W. Scott, U. S. P. 1,678,084, July 24, 1928, to Rubber Service Lab. Co.; *Chem. Abs.*, 1928, 22, 3552.  
<sup>108</sup> M. G. Shepard and H. S. Adams, U. S. P. 1,471,313, Oct. 16, 1923, to Naugatuck Chem. Co.; *Chem. Abs.*, 1924, 18, 158.

<sup>109</sup> H. Fritzsche, U. S. P. 1,864,425, June 21, 1933, to Clayton Aniline Co., Ltd.; *Chem. Abs.*, 1933, 26, 4506. British P. 326,523, 1923; *Brit. Chem. Abs. B*, 1930, 849. See also French P. 690,955, 1929, to

Thus, formaldehyde condensed with sodium anilinemethane- $\omega$ -sulphonate and crotonaldehyde condensed with sodium aniline-ethane- $\alpha$ -sulphonate,



give products with the desired properties.

#### RUBBER PRESERVATIVES

Certain amine-aldehyde combinations preserve rubber compositions from rapid deterioration. Several terms are used to denote the function of these compounds; they are known as antioxidants, anti-agers and age-retarders. The protective action of antioxidants, according to studies made by Kohman,<sup>169</sup> is a negative catalysis rather than a preferential absorption. On the other hand, Kirchhof,<sup>170</sup> in a study of aldol- $\alpha$ -naphthylamine, found that anti-agers have intense colorations with certain metallic chlorides (ferric and cupric chloride) and considered the products analogous to hæmin inasmuch as the catalytic effect was suppressed by hydrogen cyanide.

Naunton<sup>171</sup> classified antioxidants as natural, physical or chemical. The chemical antioxidants, which include the amine-aldehyde preservatives, are chiefly of use for protection against heat-induced oxidation, and serve poorly as protection against light.

Deterioration retarders from 1 mol of  $\alpha$ -naphthylamine condensed with 2 mols of acetaldehyde in an inert solvent were made by Robinson.<sup>172</sup> These products may be heated to fusion with 0.3-0.5 mol of other aromatic amines (diethylaniline, dimethylaniline,  $\beta$ -naphthylamine) forming clear, brittle resins also used with rubber as age-resistors.<sup>173</sup> Cronshaw and Naunton<sup>174</sup> combined equal proportions of  $\alpha$ - and  $\beta$ -naphthylamine and condensed the mixture with acetaldehyde in the presence of hydrochloric acid. The addition of 1.5 per cent of the product imparts good aging properties to rubber compositions.  $\alpha$ -Naphthylamines and aliphatic aldehydes may be condensed in the presence of water-soluble alcohols and acids, and the resins formed are further treated with water.<sup>175</sup> Yellowish, odorless powders are obtained which are antioxidants and do not interfere with normal vulcanization. Acetaldehyde, aldol and crotonaldehyde are examples of aldehydes employed, and the acids used are formic and acetic.

Aldol- $\alpha$ -naphthylamine was found by Winklemann and Gray<sup>176</sup> to increase the durability of rubber and to have no accelerating effect on vulcanization. This com-

Clayton Aniline Co., Ltd.; *Chem. Abs.*, 1930, 24, 4128. German P. 529,320, 1929; *Chem. Abs.*, 1931, 25, 5056.

<sup>169</sup> G. T. Kohman, *J. Phys. Chem.*, 1929, 33, 226; *Chem. Abs.*, 1929, 23, 2600.

<sup>170</sup> F. Kirchhof, *Kautschuk*, 1931, 7, 7; *Brit. Chem. Abs. B*, 1931, 262.

<sup>171</sup> W. J. S. Naunton, *Trans.Inst. Rubber Ind.*, 1930, 5, 317; *Brit. Chem. Abs. B*, 1931, 76.

<sup>172</sup> R. Robinson, British P. 316,761, 1928, to Clayton Aniline Co., Ltd.; *Brit. Chem. Abs. B*, 1927, 807.

<sup>173</sup> R. Robinson, U. S. P. 1,923,793, Aug. 22, 1933, to Clayton Aniline Co., Ltd.; *Chem. Abs.*, 1933, 27, 5577. British P. 317,205, 1928; *Brit. Chem. Abs. B*, 1929, 829. German P. 523,694, 1929; *Chem. Abs.*, 1931, 25, 5875.

<sup>174</sup> C. J. T. Cronshaw and W. J. S. Naunton, British P. 280,561, 1926, to Brit. Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1928, 22, 3318.

<sup>175</sup> British P. 352,549, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 444. British P. 333,941, 1927; *Chem. Abs.*, 1931, 25, 713. E. Riets and W. Hoffmann, German P. 539,181, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1620.

<sup>176</sup> H. A. Winklemann and E. Gray, U. S. P. 1,515,642, Nov. 18, 1924, to B. F. Goodrich & Co.; *Chem. Abs.*, 1925, 19, 420.

pound (known as "agerite resin"<sup>177</sup>) was studied by Chesnokov<sup>178</sup> who found that phenyl- $\beta$ -naphthylamine had the same action on rubber. Thermoplastic unvulcanized insulating compounds for deep-sea cables containing rubber, gutta-percha, balata and a plasticizer were preserved by Kemp and Ingmanson<sup>179</sup> with small amounts of aldo- $\alpha$ -naphthylamine, acetaldehyde-ethylenediamine<sup>180</sup> and other anti-oxidants.

By reacting aniline and acetaldehyde at low temperatures (approximately 0°C.), Sebrell<sup>181</sup> produced a rubber preservative that is not a vulcanization accelerator. Crotonaldehyde and an aromatic amine, likewise, can be used to retard rubber deterioration.

Aldehydes and diarylamines were condensed by Semon<sup>182</sup> and resinous, non-accelerating products were obtained that are used as antioxidants in vulcanized rubber and as retarders of resinification and as depressants of tack in raw rubber. The reagents used include butyraldehyde, aldol, or formaldehyde with diphenylamine, phenyl- $\beta$ -naphthylamine, dinaphthylamine or sym-diphenyl-p-phenylene-diamine. Formaldehyde or aldol also gives anti-agers by reaction with diarylalkylenediamines (e.g., diphenylethylenediamine).<sup>183</sup> Unsaturated aldehydes and aniline or  $\alpha$ -naphthylamine yield effective deterioration retarders when condensed in an acid medium.<sup>184</sup> Scott<sup>185</sup> employed 2 per cent of the reaction product of a Schiff base (e.g., crotonaldehyde-aniline) with phenol or  $\alpha$ - or  $\beta$ -naphthol in curing rubber. Iodine was utilized as a catalyst and the resulting substance was directly incorporated in the rubber mix prior to vulcanization.

Equimolecular proportions of butyraldehyde and a primary aromatic amine condensed in the presence of at least 0.03 mol of a weak organic acid per mol of aldehyde were found by Williams<sup>186</sup> to be age-resistors for rubber. Rubber contained in plants of the guayule type, after harvesting and during extraction, was treated for preservation by Spence<sup>187</sup> with a dilute solution of an amine-aldehyde condensation product.

The material formed by heating together aniline, acetone and phenol or  $\beta$ -naphthol was made by ter Horst<sup>188</sup> as an antioxidant. As an example of this investigator's procedure, 144 g. (1 mol) of  $\beta$ -naphthol, 93 g. (1 mol) of aniline, 500 g. of acetone and 2 g. of iodine are heated at 200-220°C. in a rotating iron autoclave for 24 hours. A quantity (722 g.) of a dark-brown liquid is obtained, from which the excess of acetone, the water formed in the reaction and unreacted aniline are removed by distillation. The product, a heavy oil, gave good results as an antioxidant when tested in a carbon black stock consisting of 100

<sup>177</sup> Agerite resin is prepared by the condensation of equimolecular proportions of acetalal with  $\alpha$ -naphthylamine. It is a cherry-red product, brittle at low temperatures and liquid at 100°C. (P. I. Murrill, private communication). See also R. T. Vanderbilt Co., *Vanderbilt News*, 1931, 1 (3), 4; *Chem. Abs.*, 1932, 26, 4206, and L. J. D. Healy, *Chem. Met. Eng.*, 1928, 35, 622.

<sup>178</sup> N. Chesnokov, *J. Rubber Ind. (U. S. S. R.)*, 1933, 9, 400; *Chem. Abs.*, 1934, 28, 2942.

<sup>179</sup> A. R. Kemp and J. H. Ingmanson, *British P.* 391,50, 1933, to Electrical Research Products, Inc.; *Chem. Abs.*, 1934, 28, 371.

<sup>180</sup> Known as V. G. B. See L. J. D. Healy, *Chem. Met. Eng.*, 1928, 35, 622.

<sup>181</sup> L. B. Sebrell, *Canadian P.* 282,347 and 282,348, 1928, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1928, 22, 3552. *British P.* 286,288, 1927; *Chem. Abs.*, 1929, 23, 309.

<sup>182</sup> W. L. Semon, *U. S. P.* 1,860,434, May 31, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1932, 26, 3959. *British P.* 317,786, 1929; *Brit. Chem. Abs. B.*, 1930, 1122. *Canadian P.* 308,541, 1931; *Chem. Abs.*, 1931, 25, 1705.

<sup>183</sup> P. I. Murrill and W. W. Evans, *U. S. P.* 1,755,703, April 22, 1930, to R. T. Vanderbilt Co., Inc.; *Chem. Abs.*, 1930, 24, 2918.

<sup>184</sup> C. W. Bedford, *U. S. P.* 1,777,634, Oct. 7, 1930, to B. F. Goodrich Co.; *Brit. Chem. Abs. B.*, 1931, 600.

<sup>185</sup> W. Scott, *U. S. P.* 1,859,801, May 24, 1932, to Rubber Service Lab. Co.; *Chem. Abs.*, 1932, 26, 3960.

<sup>186</sup> I. Williams, *U. S. P.* 1,908,093, May 9, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 3854.

<sup>187</sup> D. Spence, *U. S. P.* 1,753,184 and 1,753,185, April 1, 1930, to Intercontinental Rubber Co.; *Brit. Chem. Abs. B.*, 1930, 823.

<sup>188</sup> W. P. ter Horst, *U. S. P.* 1,870,880, Aug. 9, 1932, to Naugatuck Chem. Co.; *Chem. Abs.*, 1932, 26, 5787.

parts of smoked sheet, 10 parts of zinc oxide, 42 parts of carbon black, 3.25 parts of stearic acid, 3.25 parts of sulphur, 3.5 parts of pine tar and 1.25 parts of mercaptobenzothiazole. Coleman<sup>120</sup> treated aniline with formaldehyde at 40°C. for 2 hours, separated water, and added aniline hydrochloride. The mixture is then heated at 80°C. for 24 hours, the acid is neutralized and water and unreacted aniline distilled off. The product, 4,4'-diaminodiphenylmethane, or its combination with 0.5-1 mol of formaldehyde may be used to retard rubber aging. In strongly acid solution, 1 mol of aliphatic aldehyde gives rubber protective agents with 1 mol of an aromatic amine (aniline, o-, m- or p-toluidine, monomethylaniline or 4-amino-1,3-xylene).<sup>120</sup> The hexahydro-1,3,5-triazines obtained from formaldehyde and ethylamine are both accelerators and anti-agers. Cadwell<sup>121</sup> obtained the anti-aging effect by using an excess of the reagent over the amount required for vulcanization and by using a smaller proportion of sulphur.

A small quantity of the resinous or syrupy product obtained by the interaction of a mono- or polysaccharide and an amine was found by Källner<sup>122</sup> to effect age-retarding in rubber. Aldoses and ketoses may be used with aniline,  $\alpha$ - and  $\beta$ -naphthylamine, m-toluylenediamine, urea or p-aminophenol.

#### MISCELLANEOUS COMPOSITIONS

When the benzylidene derivatives of aromatic amines are heated, resin formation is observed (as already noted). Thus, for example, benzylideneaniline, heated with 25 per cent hydrochloric acid at 150°C., gave an elastic resin, insoluble in acids and alkalis but soluble in benzene and linseed oil. A similar product is obtained by heating  $\alpha$ -naphthylamine, benzaldehyde, solvent naphtha and 25 per cent hydrochloric acid together under reflux. The products are elastic and good insulators. Fillers may be added either before, during or after formation of the resins.<sup>123</sup>

The condensation of primary aromatic amines with derivatives containing active methylene groups (formaldehyde, anhydroformaldehydeaniline, anhydro-p-aminobenzyl alcohol) at a temperature below 120°C. in acid media yields polynuclear amino bases that may be used as additions to pickling acids, in the rubber industry or as starting materials for the preparation of resins.<sup>124</sup> These polynuclear bases have their nuclei directly or indirectly linked by methylene groups (present in the proportion of less than 2 methylene groups for each 2 mols of aromatic residue) and yield thermoplastic and thermohardening resins when condensed with aldehydes.<sup>125</sup> Mono- or polynuclear phenols or phenolic esters which contain active  $-\text{CH}_2$  groups have also been condensed with aromatic amines to give resins having low molecular weights.<sup>126</sup>

As an example, 1 mol of diaminodiphenylmethane in alcohol is heated with 2 mols of formaldehyde. The product is treated with aniline and glacial acetic acid and kneaded with wood flour, salicylic acid and formaldehyde. It is then dried, molded and heated.<sup>127</sup>

<sup>120</sup> C. Coleman, British P. 344,174, 1929, to Naugatuck Chem. Co.; *Chem. Abs.*, 1933, 26, 337.

<sup>121</sup> S. M. Cadwell, U. S. P. 1,626,784, May 3, 1927, to Naugatuck Chem. Co.; *Chem. Abs.*, 1927, 21, 2300. U. S. P. 1,855,236, April 26, 1933; *Chem. Abs.*, 1933, 26, 3408. British P. 240,407, 1924; *Chem. Abs.*, 1926, 20, 2363.

<sup>122</sup> S. M. Cadwell, U. S. P. 1,673,549, June 12, 1928, to Naugatuck Chem. Co.; *Brit. Chem. Abs. B*, 1928, 763.

<sup>123</sup> G. Källner, German P. 556,346, 1927, to Silesia Verein Chem. Fab.; *Chem. Abs.*, 1932, 26, 5737. British P. 291,431, 1927; *Chem. Abs.*, 1929, 23, 1303.

<sup>124</sup> H. Rauch, German P. 401,738, 1923; *J.S.C.I.*, 1925, 44, 216B.

<sup>125</sup> French P. 749,064, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 431.

<sup>126</sup> French P. 750,025, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 666. British P. 401,535, 1923; *Brit. Chem. Abs. B*, 1924, 71.

<sup>127</sup> French P. 778,530, 1934, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1935, 29, 1536.

<sup>128</sup> Swiss P. 163,552, 1933, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1934, 28, 2990. Swiss P. 166,403, 1934, addn. to 163,552; *Chem. Abs.*, 1934, 28, 5611.

The addition of between 0.5 and 1 per cent of the condensation product of acetaldehyde and aniline to oil, used in impregnating paper for the wrapping of cables, is found to prevent deterioration of the oil. Lubricating oils and transformer oils may be protected from deterioration by a similar addition. The products from other aldehydes (e.g., formaldehyde, benzaldehyde, furfural or aldol) with other amines (e.g., aniline,  $\alpha$ - and  $\beta$ -naphthylamine or ammonia) may be used for the same purpose.<sup>198</sup>

Compositions which are mixtures of organic polysulphide plastics and aldehyde-arylamine resins have been prepared. The products are obtained by dissolving the reactive halogenated hydrocarbon and alkali polysulphide in the amine and then adding the aldehyde.<sup>199</sup>

A mixture of an amine-aldehyde resin with an alkaline solution of a phenol-aldehyde condensation product in a water-miscible solvent forms a precipitate that may be used as a molding powder after neutralizing, washing and drying.<sup>200</sup> The amine-aldehyde resin is prepared by condensing the amine with aqueous formaldehyde at room temperature in the presence of water. The phenol-aldehyde product is used when in the soluble or "A" phase with a cure of 30-120 seconds on a hot-plate heated to 160°C. In electrical insulation products from phenol-aldehyde and other resins, the surface-leakage paths are reduced by applying an amine-aldehyde resin as a covering layer. The amine resin is scattered on the article during the pressing operation.<sup>201</sup>

Non-sulphonated, water-soluble amine-formaldehyde resins are applied to hides previous to tanning. The tanning process is accelerated by these compounds either alone or with dilute tanning solutions or a mixture of alum and Glauber's salt.<sup>202</sup>

Resins formed by condensing aromatic amines with aldehydes in the absence of solvents and with filling materials, catalysts, pigments and plasticizers are used in the manufacture of pressed articles.<sup>203</sup>

<sup>198</sup> A. A. Somerville, U. S. P. 1,594,983, Aug. 3, 1926, to R. T. Vanderbilt Co.; *Chem. Abs.*, 1926, 20, 3235.

<sup>199</sup> D. F. Twiss and A. E. T. Neale, British P. 420,386, 1933, to Dunlop Rubber Co., Ltd; *Brit. Chem. Abs. B*, 1935, 111.

<sup>200</sup> P. F. Schlingman and R. H. Kienle, British P. 400,698, 1933, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1934, 28, 2137.

<sup>201</sup> Allgem. Elekt.-Ges., British P. 399,738, 1933, to Int. Gen. Electric Co., Inc.; *Brit. Chem. Abs. B*, 1933, 1069.

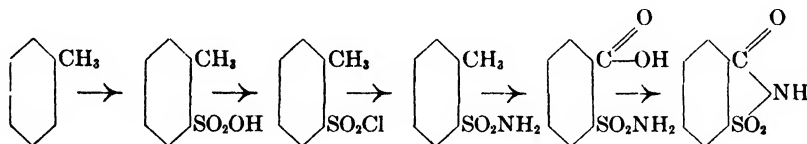
<sup>202</sup> B. Quendt, British P. 332,262, 1929; *Brit. Chem. Abs. B*, 1930, 919.

<sup>203</sup> German P. 598,657, 1934, to Allgem. Elekt. Ges.; *Chem. Abs.*, 1934, 28, 6003.

## Chapter 34

### Sulphonamide-Aldehyde Resins

The development of sulphonamide-aldehyde resins has been largely a result of efforts to utilize p-toluenesulphonamide, a by-product in the manufacture of saccharin.<sup>1</sup> The latter is made from toluene as indicated by the following series of formulas.<sup>2</sup>



Toluene when treated with an excess of chlorosulphonic acid yields first, toluene o-sulphonic acid and then toluene o-sulphonyl chloride. The treatment of this latter compound with ammonia yields toluene o-sulphonamide, which, on oxidation, is converted into o-benzoic sulphonamide, and finally into saccharin, with the loss of 1 molecule of water.<sup>3</sup>

In the sulphonation of toluene both the ortho and para sulphonic acids are formed, which by the above reaction are converted into the corresponding sulphonamides. The ortho compound on oxidation yields saccharin, whereas the oxidation product of the para compound is tasteless, and therefore of no value in this particular synthesis. Hence other uses have been sought for the p-sulphonamide.

One of the results of this search has been the production of sulphonamide-aldehyde resins. (See Fig. 117). It was found that p-toluenesulphonamide and formaldehyde in equimolecular proportions condense to a semi-solid or viscous mass, which when heated to 110°C. yields a hard colorless resin.<sup>4</sup> A mixture of o- and p-toluenesulphonamides when heated at 110-120°C. with paraformaldehyde yields a brittle resin. If p-toluene-sulphon-ethylamide is heated with formaldehyde and hydrochloric acid a soft resin is formed.

It was then found that a great number of sulphonamides can be used, including ortho-, meta- and para-toluenesulphonamides, naphthalenesulphonamide, halogenbenzene- and nitrobenzenesulphonamides and N-mono-alkyl derivatives of these sulphonamides.<sup>5</sup> The resins formed from such compounds are soluble in alcohol and acetone, giving clear varnishes and lacquers which are not affected by light. If the sulphonamides of tetrahydronaphthalene or its N-mono-substituted derivatives are condensed with formaldehyde,

<sup>1</sup> A discussion of this subject has been made by W. Herzog (*Kunststoffe*, 1926, 16, 105; *Chem. Abs.*, 1926, 20, 2910; "Die Verwertung der Nebenprodukte der Saccharinfabrikation," Ferdinand Enke, Stuttgart, 1926).

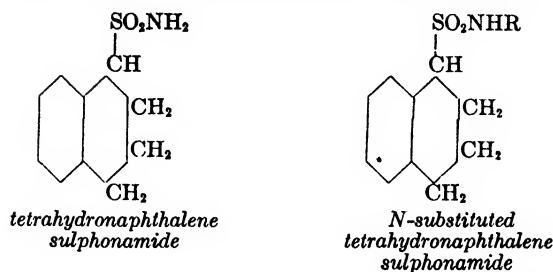
<sup>2</sup> See W. M. Cumming, I. V. Hopper and T. S. Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Co., New York, 1931, 317.

<sup>3</sup> The original work on saccharin was performed by C. Fahlberg and I. Remsen (*Ber.*, 1879, 12, 469; *J.C.S.*, 1879, 35, 628).

<sup>4</sup> German P. 359,876, 1919, to Farb. vorm. Meister, Lucius & Brünig, *J.S.C.I.*, 1923, 42, 279A.

<sup>5</sup> German P. 369,844, 1919, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 614A.





resins are obtained which have higher melting points than those from the substances named above.\*

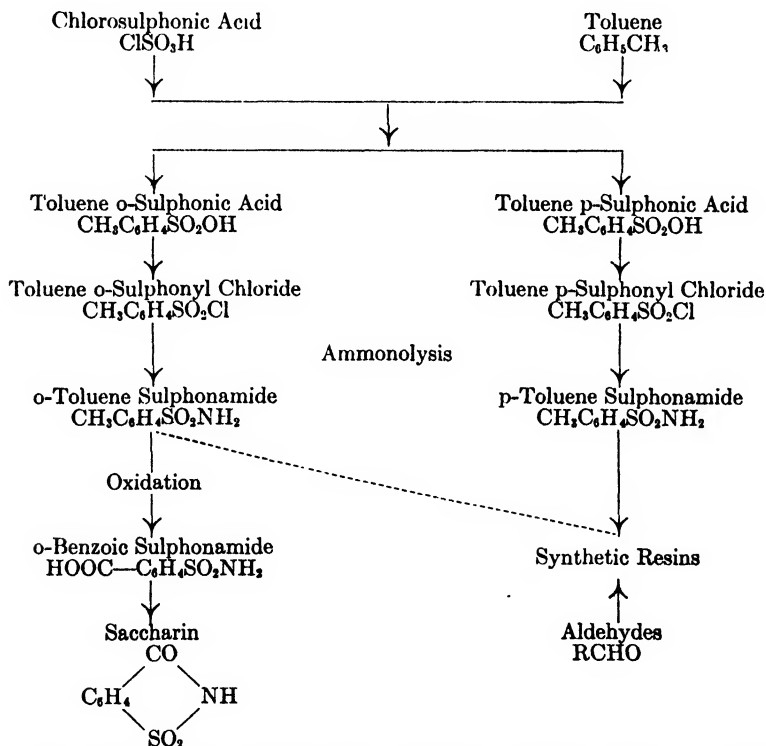


FIG. 117.—Flow Sheet for the Production of Toluene Sulphonamide as a By-Product in the Manufacture of Saccharin. Dotted line indicates that although o-toluene sulphonamide may be employed in resin-making, its principal use is the preparation of saccharin.

Sulphonamide-aldehyde resins were found to be compatible with cellulose esters and ethers and to increase the adhesion and clarity of lacquers. Moss and White<sup>7</sup> noted that ordinary p-toluenesulphonamide-formaldehyde resins were objectionable when mixed with cellulose esters because of their softness and because they con-

\* A. Steindorff and G. Balle, German P. 376,473, 1921, addition to 369,644, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 1141A.

<sup>7</sup> W. H. Moss and B. B. White, U. S. P. 1,908,159, May 9, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 3837. British P. 317,456, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 2217. Canadian P. 313,858, 1931, to Camille Dreyfus; *Chem. Abs.*, 1931, 25, 5305.

tain excess sulphonamide, which tended to form a "bloom" on the surface of films or plastics in which the resins were used. It was found that this fault could be remedied by heating the resin under reflux for 3 hours at 200-260°C. The product then has a melting point of 35-40°C. The same result can be obtained by adding to the reactants 5-10 per cent of urea.

Moss and White further noted that p-toluenesulphonamide-formaldehyde resin can be made to react with more sulphonamide to form a resin of higher melting point.\* A method used by them is as follows: Equimolecular proportions of p-toluenesulphonamide and formaldehyde are heated under reflux at 100-150°C. for 16-20 hours, yielding a soft, yellow resin. Purification with solvents and then heating in the open at 130-150°C. for 4-20 hours produces a hard, yellow resin, soluble in benzene. The addition of up to 25 per cent more p-toluenesulphonamide and further heating at 130-150°C. for 1-4 hours produces a clear, hard resin (melting at 64-75°C.) soluble in acetone, alcohol and benzene. This substance is completely compatible with cellulose acetate and is adaptable for non-blooming threads, films and molded articles. The procedure may be slightly modified by adding to the original reactants 5-10 per cent of urea.

The resin formed by using excess p-toluenesulphonamide was found to be unstable. When heated for 4-8 hours at 175°C. it changed into a dark, greenish-brown mass consisting of two crystalline substances, one melting at 140-150°C. and the other at 160-162°C. and both practically insoluble in benzene. If to the crystalline material up to 50 per cent of formaldehyde solution (40 per cent) is added and the mixture heated at 120-150°C. for from 6 to 12 hours, a soft, light brown mass is formed. Fusion of this mass in the open at 130-150°C. for 2-6 hours yields a transparent, light brown resin soluble in benzene and possessing a green fluorescence.\*

Other aldehydes besides formaldehydes have been utilized in making sulphonamide-aldehyde resins. Moss and White used furfural<sup>10</sup> and benzaldehyde.<sup>11</sup> Mixtures of aldehydes with urea, phenol, aniline or acetone have also been employed, producing complex resins.

The sulphonamides of aromatic ethers (e.g., etherified phenol, cresol, naphthol, resorcinol or pyrocatechol) may be substituted for p-toluenesulphonamide in making resins compatible with cellulose derivatives.<sup>12</sup>

Rispler, Luthy and Schilling<sup>13</sup> found that in the condensation of sulphonamides and aldehydes, the presence of acid condensing agents causes the formation of crystalline substances. For example: 100 parts of p-toluenesulphonamide are heated with 17-20 parts of paraformaldehyde at 100-150°C. until the mixture becomes a clear liquid. Then an acid condensing agent (0.1 to 3 parts of concentrated sulphuric acid or 0.5 to 6 parts of zinc chloride) is added, converting the liquid into a white, crystalline mass (m. p. 160-170°C.). A modified procedure involves addition of 20 parts of glacial acetic acid to the initial reactants at a lower temperature (60-120°C.) and the employment of more condensing agent (10 parts of either sulphuric acid or zinc chloride). Instead of paraformaldehyde, formaldehyde, trioxymethylene or polyoxymethylenes may be used. Also, other sulphonamides may be substituted which also

\* W. H. Moss and B. B. White, U. S. P. 1,873,848, Aug. 23, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 6166. British P. 338,002, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 2312. Canadian P. 319,731, 1932, to Camille Dreyfus; *Chem. Abs.*, 1932, 26, 2609.

\* W. H. Moss and B. B. White, U. S. P. 1,907,554, May 9, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 3629. British P. 338,024, 1928, addn. to 338,002, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 2313. Canadian P. 317,331, 1931, to Camille Dreyfus; *Chem. Abs.*, 1932, 26, 1461.

<sup>10</sup> W. H. Moss and B. B. White, U. S. P. 1,840,508, Jan. 12, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 1812. British P. 340,102, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 2367. Canadian P. 308,697, 1930, to Camille Dreyfus; *Chem. Abs.*, 1930, 24, 5518.

<sup>11</sup> W. H. Moss and B. B. White, U. S. P. 1,840,597, Jan. 12, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 1813. British P. 340,101, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 2367. Canadian P. 318,729, 1932, to Camille Dreyfus; *Chem. Abs.*, 1932, 26, 2608.

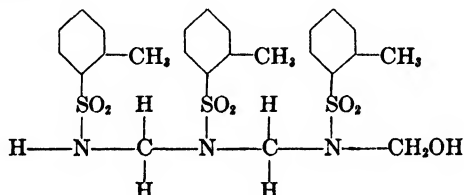
<sup>12</sup> British P. 417,795, 1934, to British Celanese, Ltd.; *Chem. Abs.*, 1935, 29, 1535.

<sup>13</sup> A. L. Rispler, M. Luthy and F. E. Schilling, British P. 349,936, 1928, to Monsanto Chemical Works; *Chem. Abs.*, 1932, 26, 5392.

give crystalline substances. Usually these products when melted will not recrystallize on cooling, but form transparent, amorphous masses. They are similar to the resins of the other investigators mentioned and can be used for the same purposes. Analogous thermohardening resins are prepared by the reaction of formaldehyde with a phenol, urea (or urea derivatives), and an aromatic sulphonamide.<sup>14</sup> The amount of sulphonamide is not less than one-half of the amount of formaldehyde used. In one example 50 parts of p-toluenesulphonamide are used with 5 parts of phenol, 25 parts of urea and 150 parts of 37 per cent formaldehyde. The resins are soluble in low-boiling solvents and are said to be resistant to light.

Walter<sup>15</sup> prepared resins, which become infusible and insoluble when subjected to heat and pressure, by condensing aldehydes with aromatic sulphonamides containing, in addition to the sulphonamido group, at least one amino group, either as a carbamido group or as an additional sulphonamido group. Examples of these include m-sulphamidobenzamide, benzene-m-disulphonamide, mixed xylenedisulphonamides, and aniline-2,4,6-trisulphonamide.

Walter and his associates<sup>16</sup> have investigated the structure of sulphonamide-aldehyde condensates. Aryldisulphonamide-formaldehyde resin can be made infusible and insoluble, whereas arylmonosulphonamide-aldehyde resin cannot. These workers stated that the arylmonosulphonamide-aldehyde resins are probably made up of 3-membered methylenemethylolarylsulphonamide groupings carrying one terminal methylol group.



The above compound, dimethylenemethylol-tri-o-toluenesulphonamide, was obtained in crystalline form from an arylmonosulphonamide resin. It was found that the arylldisulphonamide-formaldehyde resin is also built up of methylene-methylol groupings which in many cases can be converted into di-methylene-arylsulphonamides of resinous character.

Walter and Storfer obtained resins from aryl sulphonamido carboxylic acid amides by condensation with formaldehyde. These resins are hydrophilic whereas the ordinary sulphonamide resins are hydrophobic. Attempts to resinify aryl dicarboxylic acid diamides with formaldehyde were unsuccessful.

In experiments of Walter and Lutwak, resins were obtained by the action of formaldehyde on 1,3,5-benzenetrisulphonamide, and phenol-2,4-disulphonamide. Resins from benzenesulphonanilide and from p-toluenesulphonanilide were obtained only in concentrated hydrochloric acid.

Aniline-m- and p-sulphonamide were found capable of yielding hardenable resins with formaldehyde or acetaldehyde, thus indicating that reaction could be made to take place with both the phenylamino and sulphonamide groups, in accordance with the theory that two reactive groups are necessary for the formation of infusible products. Occurrence of such radicals in the ortho position or acetylation of the amino group eliminates one reactive position. Thus aniline-o-

<sup>14</sup> A. Spitzer, British P. 409,490, 1933; *Brit. Chem. Abs.* B, 1934, 591. French P. 752,231, 1933; *Chem. Abs.*, 1934, 28, 920.

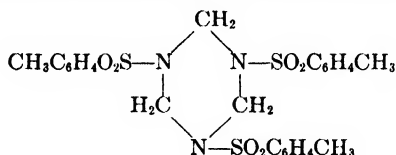
<sup>15</sup> G. Walter, British P. 375,843, 1932, to Verein. Chem. Fabr. Kreidl. Heller & Co.; *Brit. Chem. Abs.* B, 1933, 998. French P. 714,560, 1931; *Chem. Abs.*, 1932, 26, 1813. G. Walter, British P. 359,523, 1929; *Chem. Abs.*, 1933, 27, 438. German P. 549,021, 1930; *Chem. Abs.*, 1933, 27, 2321.

<sup>16</sup> G. Walter and A. Glück, *Kolloid-Beihfte*, 1933, 37, 343; G. Walter and E. Storfer, *ibid.*, 378. G. Walter and H. Lutwak, *ibid.*, 385; *Chem. Abs.*, 1933, 27, 4638.

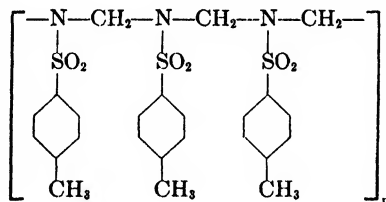
sulphonamide gave with acetaldehyde a crystalline monoethylidene compound and with formaldehyde a fusible resin. Furfural formed hardenable resins of complicated structure except in the case of acetylated derivatives, when crystalline monofurfurylene compounds were secured. Benzaldehyde reacted only with the nuclear  $\text{—NH}_2$  groups and therefore only crystalline bodies were obtained.<sup>17</sup>

Wood and Battye<sup>18</sup> prepared a light-stable, water-soluble amorphous substance by condensing a sulphonamide with formaldehyde, but with a dimethylsulphonamide a crystalline product resulted, insoluble in hot water and decomposing at about 185°C. They considered the reaction between p-aniline-sulphonamide and formaldehyde to yield a mixture of p-sulphonamide formanil ( $\text{CH}_2=\text{NC}_6\text{H}_4\text{SO}_2\text{NH}_2$ ) and p-aniline-N-methylolsulphonamide ( $\text{NH}_2\text{C}_6\text{H}_4\text{SO}_2\text{NHCH}_2\text{OH}$ ).

McMaster<sup>19</sup> concluded from his investigations that the resins from o- and p-toluenesulphonamides and trioxymethylene or formaldehyde consisted of C-N ring compounds, similar in structure to those made by Magnus-Levy<sup>20</sup> from benzenesulphonamide and formaldehyde. p-Toluenesulphonamide yielded, with formaldehyde or trioxymethylene, 1,3,5-tri-p-toluenesulphon-hexahydro-sym-triazine.

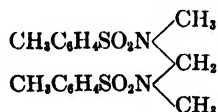


However, when Hug<sup>21</sup> carried out the same reaction in an acid medium he secured a resinous product which was considered to have the structure:



In place of the sulphonamide-aldehyde reaction, Hug used arylsulphonyl chlorides and hexamethylenetetramine, in alkaline solution, to obtain trimer bodies identical with the sulphonamide derivatives. For example, on stirring 1 mol of hexamethylenetetramine with 3 mols of p-toluenesulphonyl chloride at 60°C. in dilute sodium hydroxide solution, the above-mentioned cyclic trimer, p-toluenesulphon-hexahydro-sym-triazine, was formed.

When an alkyl derivative of p-toluenesulphonamide was used,<sup>21a</sup> no ring formation occurred. p-Toluenesulphonmethyamide yielded:



<sup>17</sup> G. Walter and H. Pollak, *Kolloid-Beihfte*, 1934, 40, 1; *Chem. Abs.*, 1934, 28, 7560. See also G. Walter and H. Engelberg, *ibid.*, 29; *Chem. Abs.*, 1934, 28, 7560.

<sup>18</sup> F. C. Wood and A. E. Battye, *J.S.C.I.*, 1933, 52, 346T.

<sup>19</sup> L. McMaster, *J.A.C.S.*, 1934, 56, 204.

<sup>20</sup> A. Magnus-Levy, *Ber.*, 1893, 26, 2143; *J.C.S.*, 1896, 64 (1), 714.

<sup>21</sup> E. Hug, *Bull. soc. chim.*, 1934, (5) 1, 990; *Chem. Abs.*, 1935, 29, 752.

<sup>21a</sup> L. McMaster, *loc. cit.*

## USES OF SULPHONAMIDE-ALDEHYDE RESINS

The resins produced by Moss and White were recommended for use in conjunction with cellulose esters or ethers in the production of lacquers, plastic compositions, artificial yarns and threads, adhesives for shatterproof glass, and photographic films. The resins can be decolorized by dissolving them in acetone, alcohol or benzene, and treating the solutions with bone black, carbon black, activated charcoal, fuller's earth or silica gel at elevated temperatures.<sup>22</sup>

For convenience in classification, the uses of these resins will now be considered under separate headings.

## COATING COMPOSITIONS AND LACQUERS

A coating composition suggested by Moss and White<sup>22</sup> consists of toluenesulphonamide-aldehyde resin (1-20 parts) and cellulose acetate (10 parts) dissolved in acetone (100 parts). Instead of using acetone alone, the solvent may consist of acetone (50 parts), benzene (25 parts), alcohol (25 parts) and diacetone alcohol (20 parts). The same proportions of resin to cellulose acetate are used if the resin employed is that formed from an excess of toluenesulphonamide, but if a toluenesulphonamide-furfural composition is used the proportions are resin (10 parts), cellulose acetate (10 parts) and acetone (100 parts).<sup>24</sup> Other ketones, containing an unsaturated carbon linkage, such as methyleneacetone or methyl isopropenyl ketone, have been employed as solvents.<sup>25</sup>

Gardner<sup>26</sup> utilized toluenesulphonamide-aldehyde resin solutions directly as lacquers without the addition of other material, though he found that the lacquer is improved by the addition of natural resins and drying oils (1 per cent of each to a solution of p-toluenesulphonamide, 50 parts, in benzene, 50 parts). By using nitrocellulose with the sulphonamide resin, Gardner obtained a lacquer which formed very tenacious films on clean metal. The lacquer was made by mixing a solution of nitrocellulose in butyl or ethyl acetate with a solution of p-toluenesulphonamide-formaldehyde resin in benzene.

This same type of mixture was used by Gardner to produce a crystalline-finish lacquer.<sup>27</sup> To 100 parts of a solution of nitrocellulose (25 per cent) in butyl acetate are added 64 parts of a solution of powdered toluenesulphonamide-aldehyde resin (25 per cent) in acetone or ethyl lactate. The principle of the crystalline effect is that the resin is very soluble in acetone but only slightly soluble in butyl acetate. The acetone, being a low-boiling solvent, evaporates first, causing the sulphonamide-aldehyde compound to crystallize out in beautiful patterns. Use of ethyl lactate instead of acetone results in slower drying and the formation of larger crystals. For improved adhesion in lacquers of the cellulose acetate type, addition of a naphthalenemonosulphonamide-aldehyde resin is recommended.<sup>28</sup>

Benzene- or xylenesulphonamide-aldehyde resins were employed by Dreyfus<sup>29</sup>

<sup>22</sup> W. H. Moss and B. B. White, Canadian P. 318,931, 1932, to Camille Dreyfus; *Chem. Abs.*, 1932, 26, 2072. British P. 342,614, 1929, and 344,413, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 4423, 4725.

<sup>23</sup> W. H. Moss and B. B. White, U. S. P. 1,907,554, May 9, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 3629.

<sup>24</sup> W. H. Moss and B. B. White, Canadian P. 319,151 and 319,152, 1932, to Camille Dreyfus; *Chem. Abs.*, 1932, 26, 2070. See Chapter 24.

<sup>25</sup> British P. 359,387, 1930, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1932, 31.

<sup>26</sup> H. A. Gardner, U. S. P. 1,564,664, Dec. 8, 1925; *Chem. Abs.*, 1926, 20, 504.

<sup>27</sup> H. A. Gardner, *Circ., Sci. Sect., Educational Bureau, Am. Paint, Varnish Mfrs. Assoc.*, 1929, 348, 327.

<sup>28</sup> British P. 416,946, 1933, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1934, 1070.

<sup>29</sup> C. Dreyfus, British P. 318,807 and 315,808, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 1754. Canadian P. 329,371 and 329,372, 1933, to Camille Dreyfus; *Chem. Abs.*, 1933, 27, 2050.

in making coating compositions or adhesives by incorporating them with cellulose esters or ethers (e.g., cellulose acetate) and then adding other synthetic resins, natural resins, or plasticizers. The mixtures are dissolved in acetates, ketones or alcohols. Brominated tricresyl phosphate is sometimes added as a fire-retardant.<sup>30a</sup>

A coating preparation similar to this was suggested by Moss and White,<sup>30</sup> consisting of cellulose acetate, toluenesulphonamide-aldehyde resin, a plasticizer (e.g., triacetin, diphenylolpropane, methylxylenesulphonamide and ethyltoluenesulphonamide) and a solvent.

A lacquer or coating composition is obtained when the mixture of cellulose derivatives and sulphonamide-aldehyde resins is dissolved in a vehicle which contains, in addition to the ordinary solvents, a glycol ether or one of its derivatives.<sup>31</sup>

Kollek<sup>32</sup> made lacquers by mixing aliphatic vinyl condensation products with sulphonamide-aldehyde resins. For instance, a clear, glass-like lacquer is formed by mixing benzenesulphonamide-formaldehyde resin with polymerized vinyl acetate (see Chapter 51). A coating material prepared by Gardner<sup>33</sup> consists of toluenesulphonamide-formaldehyde resin mixed with a natural resin or ester gum, and with chlorinated biphenyls (see Chapter 56). This mixture is incorporated with either nitrocellulose or drying oils.

A fusible coating composition is made by melting together soluble cellulose bodies and a gelatinizing agent such as p-toluenesulphonamide, or cresol derivatives.<sup>34</sup> The coats are applied to surfaces by painting, dipping, etc. A polish for surfaces lacquered with sulphonamide-aldehyde resin and cellulose preparations is made by mixing together an abrasive (tripoli), a diluent (benzene) and a softening agent (an aromatic sulphonamide).<sup>35</sup>

#### SHATTERPROOF GLASS

It is well known that shatterproof glass is made by placing between sheets of glass a layer of a cellulose ester, coated with an adhesive. One of the chief difficulties encountered in making such a product was to find a satisfactory adhesive which would be compatible with the cellulose ester and which would not be affected by light.<sup>36</sup> Gelatin, dextrin and natural gums were first utilized but they tended to discolor and become less transparent through the action of ultraviolet rays.

Gardner<sup>37</sup> noted that p-toluenesulphonamide resin, either alone or mixed with cellulose esters, possesses great resistance to decomposition by ultraviolet radiation and transmits relatively high percentages of light. He therefore proposed to use it for making laminated glass. A solution of the resin in toluene is applied to clean glass plates and, after a brief drying, the surfaces are pressed together. Also, a cement may be used, consisting of nitrocellulose (25 parts), butyl acetate (75 parts), p-toluenesulphonamide resin (50 parts) and toluene (50 parts). Other cellulose esters and ethers were suggested, and also viscose or celluloid.

<sup>30a</sup> For investigations on the durability of cellulose acetate-toluenesulphonamide lacquers see A. M. Van Heuckeroth (*Circ., Natl. Paint, Varnish, Lacquer Assoc.*, 1934, 458, 97; *Chem. Abs.*, 1934, 28, 3602).

<sup>30</sup> W. H. Moss and B. B. White, U. S. P. 1,881,219, Oct. 4, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 615. Canadian P. 329,515, 1933, to Camille Dreyfus; *Chem. Abs.*, 1933, 27, 2050. British P. 317,466, 1929; *Brit. Chem. Abs. B*, 1931, 128.

<sup>31</sup> British P. 342,144, 1930, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 4421.

<sup>32</sup> L. Kollek, German P. 578,767, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2773. French P. 721,717, 1931; *Chem. Abs.*, 1932, 26, 4190.

<sup>33</sup> H. A. Gardner, British P. 351,637, 1930; *Brit. Chem. Abs. B*, 1931, 853.

<sup>34</sup> French P. 668,239, 1929, to Lonsa Elekt.-Werke & Chem. Fabr. A.-G.; *Chem. Abs.*, 1930, 24, 1529.

<sup>35</sup> British P. 352,547, 1930, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1931, 895.

<sup>36</sup> For a discussion of safety-glass plastics see *Plastic Products*, 1934, 10, 131.

<sup>37</sup> H. A. Gardner, U. S. P. 1,762,513, June 10, 1930; *Chem. Abs.*, 1930, 24, 3873. British P. 332,234, 1929; *Brit. Chem. Abs. B*, 1930, 906. Canadian P. 302,911, 1930; *Chem. Abs.*, 1930, 24, 4910.

Moss<sup>33</sup> used a film of toluene- or ethyltoluenesulphonamide-aldehyde resin as an adhesive to bind sheets of cellulose acetate to sheets of glass in the endeavor to make a shatterproof glass. Similarly a film of benzenesulphonamide-aldehyde resin has been used by Dreyfus.<sup>30</sup> The reinforcing layer for laminated glass may consist of a cellulose ester mixed with triacetin and applied with sulphonamide-aldehyde resin as a binder.<sup>40</sup>

An intermediate layer for safety glass which does not become brittle at low temperatures is made by mixing together toluenesulphonamide-formaldehyde resin and the polymerization products of acrylic acid or its derivatives.<sup>41</sup>

Ford and McCarroll<sup>42</sup> suggested a number of substances as adhesives for the celluloid layer in safety glass, for example: cellulose nitrate, formaldehyde-toluene-sulphonamide resin, camphor and tricresyl phosphate, vinyl acetate, formaldehyde-toluenesulphonamide resin and dibutyl phthalate, and other cellulose esters, resins, and plasticizers.

Fragile articles (glass or ceramic) may be reinforced by applying to them an external coating (0.005-0.03 inch thick) of toluenesulphonamide-aldehyde resin, either alone, or mixed with other resins and with cellulose esters or ethers.<sup>43</sup>

### PLASTICS

Sulphonamides were perhaps first used by Schmidt<sup>44</sup> to plasticize cellulose esters. Nitrocellulose was mixed with p-toluenesulphonamide to form films and to act as a substitute for camphor in making celluloid. Lindsay<sup>45</sup> made a plastic product by incorporating various sulphonamides and triphenyl phosphate with acetylcellulose in acetone solution, adding methyl alcohol, and allowing the mixture to gelatinize.

A study of sulphonamide derivatives as plasticizers for acetyl cellulose was made by Carswell.<sup>46</sup> Experiments were performed on retentivity, light-fastness, tensile strength and weather-resistance of the plastic mixtures of eight different aryl sulphonamide derivatives with the acetyl cellulose. The p-toluene methylene sulphonamide (a resinous substance made by condensing p-toluenesulphonamide with formaldehyde) proved superior to any of the sulphonamides not combined with formaldehyde. See Table 34. Bender<sup>47</sup> reported that this same substance was of value in plasticizing phenol-formaldehyde resins.

Dreyfus<sup>48</sup> mixed sulphonamides with cellulose esters and ethers for making pressed or molded articles, e.g., phonograph records or electric insulators. A blend of powdered cellulose acetate (100 parts) and p-toluenesulphonamide (45-55 parts) is melted and run into sheets, which are then ground to powder and incorporated with a filling material (180-200 parts), e.g., lampblack, ferric oxide or barium sulphate. This composition is kneaded on hot rolls and then pressed or molded

<sup>33</sup> W. H. Moss, U. S. P. 1,953,971, Apr. 10, 1934, to Celanese Corp. of America; *Chem. Abs.*, 1934, 28, 3857. Canadian P. 317,726 and 318,145, 1931, to Camille Dreyfus; *Chem. Abs.*, 1932, 26, 1409, 1741.

<sup>30</sup> C. Dreyfus, British P. 315,807 and 315,808, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 1784. See H. Dreyfus, British P. 326,520, 1929; *Brit. Chem. Abs. B*, 1930, 558.

<sup>40</sup> British P. 341,890, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1931, 395.

<sup>41</sup> French P. 724,002, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4929.

<sup>42</sup> H. Ford and R. H. McCarroll, British P. 365,823, 1930, to Ford Motor Co., Ltd.; *Chem. Abs.*, 1933, 27, 3260.

<sup>43</sup> British P. 345,748, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1932, 26, 574.

<sup>44</sup> A. Schmidt, U. S. P. 753,335, Apr. 26, 1904, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1904, 23, 558. British P. 25,434, 1899; *J.S.C.I.*, 1901, 20, 62. German P. 122,372, 1899; *Chem. Zentr.*, 1901, 2, 328.

<sup>45</sup> W. G. Lindsay, U. S. P. 1,041,113, Oct. 15, 1912, to the Celluloid Co.; *J.S.C.I.*, 1912, 31, 1075.

<sup>46</sup> T. S. Carswell, *Ind. Eng. Chem.*, 1929, 21, 1176.

<sup>47</sup> H. L. Bender, U. S. P. 1,650,109, Nov. 11, 1927, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 505.

<sup>48</sup> C. Dreyfus, U. S. P. 1,595,506, Aug. 10, 1926, to American Cellulose & Chem. Mfg. Co., Ltd.; *Chem. Abs.*, 1926, 20, 3349. See H. Dreyfus, British P. 132,283 and 133,353, 1918, and 154,334, 1919; *J.S.C.I.*, 1919, 38, 890A; 1920, 39, 14A; 1921, 41, 43A.

TABLE 34.—*Sulphonamide Derivatives as Plasticizers for Acetyl Cellulose.*

Derivative	Reten- tivity <sup>a</sup> Per Cent	Light- Fastness <sup>b</sup> Hours	Tensile Strength Kilograms/sq cm.			Weather- Resistance Condition after 5 Weeks
			Plasticizer in Film			
			25%	50%	100%	
p-Toluenesulphonamide . . . . .	30		408			
Benzene methyl sulphonamide . . . . .	100+	630	453	320	80	Poor
Benzene ethyl sulphonamide . . . . .	100+	724	414	290	115	Fair
p-Toluene methyl sulphonamide . . . . .	40	1140	460			Failed
p-Toluene ethyl sulphonamide . . . . .	40	1534	380	360		Poor
Xylene methyl sulphonamide . . . . .	100	532	475	350	350	Failed
p-Toluenesulphonanilide . . . . .	70	39	335	383		Poor
p-Toluene methylene sulphon- amide . . . . .	200	About 2000	660	408	349	Good
No plasticizer . . . . .	...	.	335			...

<sup>a</sup> Retentivity is defined as the per cent of plasticizer which can be incorporated in acetyl cellulose without "frosting."

<sup>b</sup> Light-fastness is expressed as the time of exposure of a 0.4 mm film in the Fade-O-Meter before the appearance of a slight discoloration.

into desired shapes. Dreyfus, Cameron and Schneider<sup>49</sup> made a similar plastic mixture with cellulose acetate, p-toluenesulphonamide, p-toluenesulphonimide, diethyl phthalate and rosin. A plastic material for phonograph records used by Rutstein<sup>50</sup> consists of cellulose acetate plasticized with an alkyltoluenesulphonamide and triphenyl phosphate together with shellac, cotton flock and fillers.

Moss<sup>51</sup> prepared a molding composition from cellulose acetate (30 parts), toluenesulphonamide-aldehyde resin (45 parts), vinyl acetate resin (100 parts), diethyl phthalate (10 parts), acetone (400 parts), benzene (100 parts), ethyl acetate (100 parts) and dioxane (100 parts). Moss and White<sup>52</sup> found that diphenylol propane, mono-methylxylene-sulphonamide, ethyl toluenesulphonamide and triacetin are good plasticizers for mixtures of cellulose acetate and toluenesulphonamide-aldehyde resins. Among other plasticizers which have been suggested are N-alkyl sulphonamides of o-dichlorobenzene.<sup>52a</sup>

Plastics made of cellulose derivatives and sulphonamide-aldehyde resins can be improved, according to Bren,<sup>53</sup> by incorporating urea (see Chapter 32), thiourea, or guanidine. The plastic material comprises a cellulose derivative, a sulphonamide-aldehyde resin (from 10 to 150 per cent of the amount of cellulose derivative) and a urea (8-50% of the equivalent of aldehydes present).

A transparent plastic material has been made by Walsh<sup>54</sup> by adding plasticizers to a toluenesulphonamide-aldehyde resin melting below 100°C. but above room temperature. With added pigments the composition can be used for making imita-

<sup>49</sup> C. Dreyfus, W. M. Cameron and G. Schneider, U. S. P. 1,943,214, Feb. 2, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 1731.

<sup>50</sup> L. Rutstein, U. S. P. 1,727,040, Sept. 3, 1929; *Chem. Abs.*, 1929, 23, 5284.

<sup>51</sup> W. H. Moss, Canadian P. 318,758, 1932, to Camille Dreyfus, *Chem. Abs.*, 1932, 26, 2052.

<sup>52</sup> W. H. Moss and B. B. White, U. S. P. 1,881,219, Oct. 4, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 615. British P. 317,454, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 2292.

<sup>52a</sup> L. P. Kyriles, U. S. P. 1,993,722, March 5, 1935, to Monsanto Chem. Co.; *Chem. Abs.*, 1935, 29, 2546.

<sup>53</sup> B. C. Bren, U. S. P. 1,961,579, June 5, 1934, to Du Pont Viscoloid Co.; *Chem. Abs.*, 1934, 28, 4024.

<sup>54</sup> Canadian P. 333,379, 1933, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 4670.

<sup>54</sup> J. F. Walsh, U. S. P. 1,912,554, June 6, 1933, to Celluloid Corp.; *Chem. Abs.*, 1933, 27, 4365.



tion food articles. Walsh and Caprio<sup>55</sup> have made preparations consisting of a cellulose ester and a plasticizer (e.g., triphenyl phosphate), employing toluenesulphonamide-aldehyde resins (4-20 per cent of the weight of plasticizer) to prevent the exudation of the softener.

Sulphonamide-aldehyde resin may be used as a binder for inorganic compounds. For instance very durable marble objects can be made by fusing the resin with twice its weight of powdered marble and molding the mixture into any desired shape.<sup>56</sup>

#### OTHER USES

Toluenesulphonamide-aldehyde resins were employed by Gardner to deluster artificial silk so that it will more nearly resemble natural silk.<sup>57</sup> The resin is mixed in with the cellulose spinning-solution, and as the filaments form, the resin penetrates the filaments, rendering them opalescent. By using condensed aldehydes in addition to the resin, a much stronger filament is formed without sacrifice of softness. A typical spinning-solution consists of nitrocellulose (100 parts), p-toluenesulphonamide-formaldehyde resin (3 parts), paraformaldehyde (1 part), ether (200 parts) and alcohol (200 parts).

For the formation of threads from alkaline cellulose solution about 5 per cent (based on the weight of cellulose) of p-toluenesulphonamide-formaldehyde resin is dissolved in caustic soda and mixed intimately with the basic cellulose.<sup>58</sup> Threads and yarns produced from this mixture are said to have greater resistance to water than have ordinary viscose threads. If the viscose solution is to be made into films, from 10 to 20 per cent of resin is added. The films then possess improved electric resistance and water-repellent qualities. Thus ordinary cellophane is improved in resistance to ingress of moisture from air by the presence of this resin. These special films are useful for wrapping pipes to prevent corrosion, or as an insulating wrapping for telephone cables. In cases where the cloudy effect produced by the resin is undesirable it may be removed by passing the film over hot rolls.

In place of incorporating the alkaline resin solution in the cellulose, the transparent films from the latter can be coated with the liquid, dried and washed to remove the alkali. This same treatment is adaptable for waterproofing paper, wood and concrete. A composition containing 100 parts of toluenesulphonamide resin, 8 parts of sodium hydroxide and 92 parts of water has proved satisfactory. Addition of barium sulphate or similar pigments is recommended for the preparation of a cold water paint.<sup>59</sup>

Gardner has also increased the electrical resistance of films of regenerated cellulose by applying to their surfaces coatings of sulphonamide-aldehyde resin and cellulose esters.<sup>60</sup> In insulating tests an ordinary regenerated cellulose film 0.87 mil in thickness had a volume resistivity of 125 megohm-inches. The same film coated on each side with a resin-cellulose ester composition so that the total thickness was 1.52 mils had a volume resistivity of 1,500,000 megohm-inches. The coating used in this case consisted of cellulose acetate (5 parts), toluenesulphonamide-formaldehyde resin (5 parts), ethyl lactate (25 parts) and acetone (65 parts).

Lahousse<sup>61</sup> used p-toluenesulphonamide to decrease the viscosity of metallic

<sup>55</sup> J. F. Walsh and A. F. Caprio, U. S. P. 1,930,069, Oct. 10, 1933, to Celluloid Corp.; *Chem. Abs.*, 1934, 28, 271.

<sup>56</sup> French P. 731,431, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 331.

<sup>57</sup> H. A. Gardner, U. S. P. 1,768,401, June 24, 1930 and 1,864,428, June 21, 1932; *Chem. Abs.*, 1930, 24, 4392; 1932, 26, 4471.

<sup>58</sup> H. A. Gardner, U. S. P. 1,864,426 and 1,864,427, June 21, 1932; *Chem. Abs.*, 1932, 26, 4470, 4471.

<sup>59</sup> H. A. Gardner, U. S. P. 1,984,368, Dec. 18, 1934; *Chem. Abs.*, 1935, 29, 854.

<sup>60</sup> H. A. Gardner, U. S. P. 1,786,340, Dec. 23, 1930; *Chem. Abs.*, 1931, 25, 849.

<sup>61</sup> J. E. G. Lahousse, U. S. P. 1,802,619, Apr. 28, 1931; *Chem. Abs.*, 1931, 25, 3746. See Chapter 37.

resinates for the impregnation of fibrous bodies to form insulating material. As an example, 10 kg. of p-toluenesulphonamide is heated to 150°C., 90 kg. rosin added and the temperature raised to 170°C. Zinc oxide is then introduced in small amounts and the temperature further increased to 185-190°C. Paper condensers and other articles are submerged in the molten mixture for 4-5 hours at 150-200°C. After cooling to 120°C., the impregnated object is removed.

Dreyfus and others<sup>32</sup> produced artificial bristles, horsehair or straw from solutions of cellulose esters and synthetic or natural resins. For instance, a thorough mixture of cellulose acetate (33.7 parts), toluenesulphonamide-formaldehyde resin (2.1 parts), acetone (54.6 parts) and water (9.6 parts) is spun into a drying atmosphere at 55-87°C. p-Toluenesulphonamide-formaldehyde resin was used by Seel<sup>33</sup> to coat the rear side of photographic films to render them non-static. A mixture of o- and p-toluenesulphonamide-formaldehyde resins has been employed by Wedger<sup>34</sup> as a softening agent in a cellulose acetate cement for uniting shoe parts.

#### MISCELLANEOUS REACTIONS OF SULPHONAMIDES

The reactions noted here do not involve sulphonamide-aldehyde condensations but they are included to suggest other possible sources of resins from sulphonamides or their derivatives.

A product useful as a plasticizing agent has been prepared by Carswell and Gump<sup>35</sup> by the action of an acetylating agent on a sulphonamide derivative. Acetyl chloride or acetic anhydride acts on an aryl sulphonamide in which one of the free hydrogen atoms attached directly to the nitrogen atom is replaced by a hydrocarbon residue. In studies on the action of benzenediazonium chloride on p-toluenesulphonamide in a cold alkaline solution, Key and Dutt<sup>36</sup> found that the reaction proceeded very slowly, producing a brownish red resinous mass soluble in most organic solvents.

In their investigation of benzenesulphonylguanidines, Clarke and Gillespie<sup>37</sup> found that arginine reacts with benzenesulphonylchloride in sodium hydroxide solution, forming a gummy mass (dibenzenesulphonylarginine). Esterification of this material with butyl alcohol produced a colorless resin.

Aromatic sulphonylchlorides were employed by Pfister<sup>38</sup> to esterify gum accroides (see Chapter 38). The natural gum, as it occurs, is highly acid in character, whereas the resin produced by esterification is neutral, and can be used in varnishes. The resin from gum accroides and p-toluenesulphonylchloride is a tough mass which can be dried and powdered, and is soluble in benzene and in butyl acetate. Melamid<sup>39</sup> obtained resins of high melting point by the reaction of aromatic sulphonylchlorides on soft pitch or anthracene oil. For instance, soft coal-tar pitch (100 parts) is heated with sufficient aqueous soda to neutralize acidity and then cooled. A benzene solution of p-toluenesulphonylchloride is added, and the mixture is stirred for 12 hours. The benzene solution is then separated from the aqueous layer, washed with water until neutral, dried over calcium chloride

<sup>32</sup> C. Dreyfus, W. Whitehead and H. W. Kuhl, U. S. P. 1,930,220, Oct. 10, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1934, 28, 323. C. Dreyfus, British P. 342,340, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1931, 388.

<sup>33</sup> P. C. Seel, U. S. P. 1,687,041, Oct. 9, 1928, to Eastman Kodak Co.; *Chem. Abs.*, 1928, 22, 4394.

<sup>34</sup> W. H. Wedger, British P. 399,525, 1933, to Boston Blacking Co., Ltd.; *Chem. Abs.*, 1934, 28, 1834.

<sup>35</sup> T. S. Carswell and W. Gump, U. S. P. 1,916,604, July 4, 1933, to Monsanto Chem. Co.; *Chem. Abs.*, 1933, 27, 4541.

<sup>36</sup> A. Key and P. K. Dutt, *J.C.S.*, 1928, 2039.

<sup>37</sup> H. T. Clarke and H. B. Gillespie, *J.A.C.S.*, 1932, 54, 1964.

<sup>38</sup> K. H. T. Pfister, U. S. P. 1,608,421, Nov. 23, 1926, to Röh m & Haas Co.; *Chem. Abs.*, 1927, 21, 333.

<sup>39</sup> M. Melamid, British P. 133,712 and 133,713, 1919; *Chem. Abs.*, 1920, 14, 852. German P. 380,835, 1918.

and vacuum-distilled, leaving the resin as a residue. Analogous resins are obtained from the action of aromatic sulphonylchlorides on the salts of resinic, humic, or lignoceric acids.

Attempts to dibrominate 2-p-toluene-sulphonamidobiphenyl resulted in the formation of gummy masses containing 3,5-dibromo-2-aminobiphenyl in experiments performed by Bell.<sup>70</sup> Much tarry material was formed when Orndorff and Shapiro<sup>71</sup> attempted to utilize dehydrating agents such as sulphuric acid or stannous chloride to increase the yield of hydroquinolsulphonephthalein from the action of o-sulphobenzoic anhydride and hydroquinol. Phillips<sup>72</sup> obtained some black, tarry material as a by-product in making ethyl p-toluenesulphinate from p-toluenesulphiny chloride and ethyl alcohol, and in making 2-octyl-p-toluenesulphinate from p-toluenesulphiny chloride and *l*-2-octanol.

<sup>70</sup> F. Bell, *J.C.S.*, 1930, 1071

<sup>71</sup> W. R. Orndorff and C. V. Shapiro, *J.A.C.S.*, 1928, 50, 1730.

<sup>72</sup> H. Phillips, *J.C.S.*, 1925, 127, 2552.

## Chapter 35

### Miscellaneous Nitrogen-Containing Resins

#### Nitro Resins

Although resinous bodies are frequently encountered in the nitration of organic substances, not many of them have been adequately described, and very few have appeared to find commercial application. Some of these resins possess unattractive colors and odors and many are unstable, decomposing (in some cases rather violently) when heated. In addition to nitro resins, materials of a resinous nature from various aliphatic and aromatic nitrogen compounds and from heterocyclic compounds are also considered in this chapter.

#### RESINS PRODUCED DURING NITRATION OF HYDROCARBONS

Schaarschmidt and Raack<sup>1</sup> obtained resinous material when attempting to nitrate benzene with a mixture of nitrosyl chloride and aluminum chloride at 60-80°C. The yield of resin at 80°C. was 10 times that at 60°C. An explanation proposed for the reaction is that a complex,  $2\text{AlCl}_3 \cdot 3\text{C}_6\text{H}_6 \cdot 3\text{NOCl}$ , is formed, which decomposes to hydrochloric acid, nitrosobenzene and aluminum chloride, the nitrosobenzene then reacting with benzene to form resins. Xylene and mesitylene yield resinous material when treated with nitrogen tetroxide at room temperature.<sup>2</sup> A mixture of 80 g. of m-xylene and 23 g. of dry nitrogen tetroxide was allowed to stand for 15 days. A thick oily layer slowly settled out. This viscous mass was steam distilled, yielding 14 g. of a dark resin. Similar treatment of 70 g. of mesitylene with 7.6 g. of nitrogen tetroxide gave 4.5 g. of a dark brown, brittle substance.

In the nitration of durene (1,2,4,5-tetramethylbenzene) in chloroform solution, Smith and Dobrovolsky<sup>3</sup> observed that unless the chloroform solution is neutralized as soon as possible after nitration, considerable amounts of red tar are formed. Herzenberg and Ruhemann<sup>4</sup> obtained from brown-coal tar a homologue of naphthalene (presumably 1,4- or 2,4-methyl isopropyl naphthalene) which, when heated for several days under reflux with dilute nitric acid, was converted into a viscous oil, solidifying to a resinous mass when cooled.

Stilbene is readily attacked by nitrogen pentoxide, forming sticky, brown plastic masses.<sup>5</sup> Likewise, tarry products result from the action of oxides of nitrogen on phenanthrene.<sup>6</sup> 6-Acetyltetralin when treated with nitric acid yields crude acetyl nitrotetralin, a dark brown resin.<sup>7</sup> Resinous or tarry materials have been formed in the nitration of o-nitrotoluene-p-sulphonyl-p-anisidine,<sup>8</sup> 4-p-toluenesulphon-

<sup>1</sup> A. Schaarschmidt and M. Raack, *Ber.*, 1925, 58, 348; *Chem. Abs.*, 1925, 19, 1567.

<sup>2</sup> A. Schaarschmidt and E. Smolla, *Ber.*, 1924, 57, 38; *Chem. Abs.*, 1924, 18, 2138.

<sup>3</sup> L. I. Smith and F. J. Dobrovolsky, *J.A.C.S.*, 1926, 48, 1420.

<sup>4</sup> J. Herzenberg and S. Ruhemann, *Ber.*, 1927, 60, 889; *Chem. Abs.*, 1927, 21, 2122.

<sup>5</sup> L. B. Haines and H. Adkins, *J.A.C.S.*, 1925, 47, 1423.

<sup>6</sup> M. A. Iljinaki and B. V. Mixarov, *J. Chem. Ind. (Moscow)*, 1928, 5, 469; *Brit. Chem. Abs. B.*, 1928, 790.

<sup>7</sup> W. Borsche and H. Bodenstein, *Ber.*, 1926, 59, 1915; *Chem. Abs.*, 1927, 21, 84.

<sup>8</sup> F. Reverdin, *Helv. Chim. Acta*, 1924, 7, 567; *Chem. Abs.*, 1924, 18, 2142.

methylamidobiphenyl<sup>9</sup> and ethyl-bis-(4-aminophenyl)-methane hydrochloride<sup>10</sup> and in the nitrosation of 3,5-dichlorodimethylaniline.<sup>11</sup> In the nitration of m-aldehydophenyl carbonate to 4-nitro-3-aldehydophenyl carbonate, Mason<sup>12</sup> obtained tarry products. Attempts to nitrate p-cresol with nitrogen peroxide have produced resinous material.<sup>13</sup>

The nitration of triphenylcarbinol and of triphenylacetone nitrile yields amorphous, tar-like nitro derivatives.<sup>14</sup> Resinous products are also formed by the nitration of 4,4'-diethylureidobiphenyl.<sup>15</sup> Trimethylolethylmethane trinitrate,  $C_8H_6C(CH_3)_3(ONO_2)_3$ , is a waxy compound melting at 48°C. and is explosive in nature. These properties have suggested the use of the substance as a coating material for explosives, protecting them from moisture and at the same time increasing their sensitiveness.<sup>16</sup>

In the experiments of Fittig<sup>17</sup> the addition of acetone in small portions to fuming nitric acid yielded a yellow, viscid explosive oil exhibiting the properties of a nitro compound. Hydrogen sulphide and ammonium sulphide decomposed the compound, forming brown tarry liquids. The nitration of mesityl oxide yielded a brown, tough resin soluble in alcohol. One of the products of the action of nitrosyl chloride on acetone is a yellow oil (possibly phorone dinitrosochloride) which resinifies easily.<sup>18</sup>

Treatment of 3-4-dichloroacetophenone with a mixture of fuming nitric and concentrated sulphuric acids at 15°C. has resulted in resinous material.<sup>19</sup> Gummy products are obtained in the nitration of benzoin unless the conditions are carefully regulated.<sup>20</sup> Phenylcyclohexanone when treated with ethyl nitrite and potassium ethylate in ethyl alcohol at 0°C. formed a yellow oil.<sup>21</sup> Ether extraction of this oil left a residual orange-red liquid which, when slightly acidified with sulphuric acid, yielded a yellow wax. The ether extract of the yellow oil (mentioned above) gives on evaporation and further extraction a vitreous mass. Various glassy materials resulted on similar treatment of phenylcyclohexanone with nitrous vapors obtained by the action of nitric acid on arsenious oxide.

In the nitration of methyl cinnamylidenemalonate, a yellow solid was formed which decomposed to a semi-solid gum when placed over phosphorus pentoxide.<sup>22</sup> Nitric acid caused the resinification of diterpenes, obtained by Ikeda<sup>23</sup> from borneol by treatment with zinc chloride in benzene; and tarry material resulted when d-neomenthylamine was treated with nitrous acid.<sup>24</sup> The oxidation of anethole (p-propenylanisole) with nitric acid and mercuric nitrate in acetic acid solution produced anisaldehyde, anisic acid and a resinous substance<sup>25</sup> (35 per cent).

Nitro compounds frequently form resins when oxidized. The tar obtained on oxidizing o-nitrobenzylmalonate<sup>26</sup> with potassium permanganate and the formation of complex amorphous substances in the oxidation of m-dinitro- and sym-trinitrobenzene<sup>27</sup> with mercuric oxide are examples. Likewise, the reduction of

<sup>9</sup> F. Bell and P. H. Robinson, *J.C.S.*, 1927, 1129.

<sup>10</sup> S. C. Hussey, C. S. Marvel and F. D. Hager, *J.A.C.S.*, 1930, 52, 1125.

<sup>11</sup> H. H. Hodgson and J. S. Wignall, *J.C.S.*, 1927, 2221.

<sup>12</sup> F. A. Mason, *J.C.S.*, 1925, 127, 1197.

<sup>13</sup> A. Purgotti, *Ann. ist. super. agrar. Portici*, 1929, (3) 3, 41; *Chem. Abs.*, 1931, 25, 3632.

<sup>14</sup> D. Vorländer, *Ber.*, 1925, 58, 1893; *Chem. Abs.*, 1926, 20, 584.

<sup>15</sup> M. H. Werther, *Rec. trav. chim.*, 1933, 52, 657; *Brit. Chem. Abs. A*, 1935, 945.

<sup>16</sup> C. P. Spaeth, Canadian P. 340,401, 1934, to Canadian Industries, Ltd.; *Chem. Abs.*, 1934, 28, 3906.

<sup>17</sup> R. Fittig, *Ann.*, 1859, 110, 28; "Gmelin's Handbook of Chemistry," Translation of H. Watts, Cavendish Society, London, 1860, XIII, 463, 472.

<sup>18</sup> E. V. Lynn and F. A. Lee, *J. Am. Pharm. Assoc.*, 1927, 16, 309; *Brit. Chem. Abs. A*, 1927, 544.

<sup>19</sup> E. Roberts and E. E. Turner, *J.C.S.*, 1927, 1855.

<sup>20</sup> F. D. Chattaway and E. A. Coulson, *J.C.S.*, 1928, 1083.

<sup>21</sup> R. Poggi and V. Guastalla, *Gazz. chim. ital.*, 1931, 61, 405; *Chem. Abs.*, 1932, 26, 104.

<sup>22</sup> J. W. Baker and A. Eccles, *J.C.S.*, 1927, 2125.

<sup>23</sup> T. Ikeda, *Sci. Papers, Inst. Phys. Chem. Research (Tokyo)*, 1923, 7, 48; *Chem. Abs.*, 1923, 22, 3157.

<sup>24</sup> J. Read and G. J. Robertson, *J.C.S.*, 1927, 2173.

<sup>25</sup> R. Horiuchi and S. Uyeda, *J. Chem. Soc. Japan*, 1924, 45, 308; *Chem. Abs.*, 1925, 19, 1081.

<sup>26</sup> J. W. Baker and A. Eccles, *loc. cit.*

<sup>27</sup> H. H. Hodgson and E. W. Smith, *J.C.S.*, 1930, 2035.

nitration products often leads to resins and tars. For instance, resinous material has been obtained in the reduction of m-dinitrobenzene,<sup>33</sup> 2,4'-dinitrobiphenyl<sup>34</sup> and the nitration products of acetylene.<sup>35</sup> In the reduction of nitrobenzaldehyde thioether to the corresponding amino compound, an insoluble by-product is obtained. The aminobenzaldehyde thioether itself resinifies on standing.<sup>31</sup>

Resinous substances have been formed by the action of alcoholic potash on 6-nitro-7-methyl-2,4-bistrichloromethylbenzodioxin<sup>36</sup> and on crude methyl-m-nitrobenzylmalonate.<sup>37</sup> Alcoholic ammonia splits off hydrogen cyanide from o-nitrocinnamylglycolyl nitrile,  $O_2NC_6H_4CH=CHCH(OH)CN$ , and the rest of the molecule resinifies.<sup>38</sup>

#### CONDENSATIONS OF NITRO COMPOUNDS

In contact with potassium bicarbonate, 1-nitro-1-propene polymerizes to a yellow-brown solid soluble in acetic acid and in caustic soda.<sup>39</sup> 1-Nitro-1-butyne on exposure to the air is converted into a resinous mass.<sup>40</sup> Extensive resinification takes place when nitro derivatives of stilbene are exposed to ultraviolet light.<sup>41</sup> Similarly, resinous material has been reported from ultraviolet-light- or sunlight-exposure of nitropiperonal,<sup>42</sup> an alcohol solution of 3-chloro-4-nitrosophenol<sup>43</sup> and a chloroform solution of p-methoxy cinnamylidene-m-nitroacetophenone.<sup>44</sup>

Nitro derivatives have sometimes been condensed with aldehydes to form resinous substances. For instance, in the presence of piperidine, 4,6-dinitro-m-xylene condenses with salicyl-, bromosalicyl- and p-dinitroamino-benzaldehyde.<sup>45</sup>

Resins have been produced in the author's laboratory by condensing technical p-nitrochlorobenzene (m.p. 81-82°C.) with aldehydes. Acid reducing agents were found to be the best catalysts. Paraformaldehyde and p-nitrochlorobenzene, boiled for ten minutes with alcoholic hydrochloric acid and metallic zinc, give a dark, fusible resin (97 per cent yield) which is still fusible after 12 hours heating. If aqueous hydrochloric acid is employed instead of the alcoholic solution no resinification occurs. However, the aqueous solution permits resinification when furfural is used in place of paraformaldehyde. In this case the dark resin obtained is soluble but not fusible.

An aqueous solution of ammonium chloride, substituted for the hydrochloric acid, can be used successfully with paraformaldehyde. A rubbery mass is formed when equal parts of p-nitrochlorobenzene, paraformaldehyde and zinc dust are refluxed for one hour in an aqueous ammonium chloride solution. Heating this mass on a hot plate converts it into a dark, infusible resin. The production of the resin is accelerated by the addition of hexamethylenetetramine. In fact, the latter itself will condense with p-nitrochlorobenzene. Hexamethylenetetramine (25 parts) in aqueous solution refluxed with p-nitrochlorobenzene (50 parts) for 1 hour produced a dark, fusible body (70 parts). Heating on a hot plate changed

<sup>33</sup> H. Adkins and R. Conner, *J.A.C.S.*, 1931, 53, 1091.

<sup>34</sup> G. T. Morgan and L. P. Walls, *J.S.C.I.*, 1931, 50, 94T.

<sup>35</sup> A. Quilico and M. Freri, *Gazz. chim. ital.*, 1929, 59, 930; 1930, 60, 721; 1931, 61, 484; *Chem. Abs.*, 1930, 24, 3484; 1931, 25, 1947; 1933, 26, 484.

<sup>36</sup> H. H. Hodgson and H. G. Beard, *J.C.S.*, 1927, 9427.

<sup>37</sup> F. D. Chattaway and F. Calvet, *J.C.S.*, 1928, 1093.

<sup>38</sup> J. W. Baker and A. Eccles, *J.C.S.*, 1927, 2128.

<sup>39</sup> G. Heller, *J. prakt. Chem.*, 1923, 106, 1; *Chem. Abs.*, 1923, 17, 3867.

<sup>40</sup> E. Schmidt and G. Rutz, *Ber.*, 1923, 51, 3147.

<sup>41</sup> J. Loevenich, J. Koch and U. Pucknat, *Ber.*, 1930, 63, 636; *Chem. Abs.*, 1930, 24, 3211.

<sup>42</sup> R. Stoerner and H. Oehlert, *Ber.*, 1932, 55, 1232; *J.C.S.*, 1932, 122 (1), 647.

<sup>43</sup> J. B. Bailey and M. S. Klemm, *J.A.C.S.*, 1923, 50, 2714.

<sup>44</sup> W. H. Hodgson and A. Kershaw, *J.C.S.*, 1929, 1544.

<sup>45</sup> M. Gina, *Gazz. chim. ital.*, 1925, 55, 267; *Chem. Abs.*, 1926, 20, 749.

<sup>46</sup> P. Rugli, A. Zimmermann and B. Thouray, *Helv. Chim. Acta*, 1931, 14, 1280; *Chem. Abs.*, 1932, 26, 3177.

this to an infusible product soluble in water, alcohol and alcohol-benzene mixture (yield 35 per cent of original p-nitrochlorobenzene).

According to Korczynski<sup>42</sup> the resin-formation occurring in the condensation of di- or trinitrophenol with diphenylcarbamide chloride is a result of the photo-sensitiveness of the product. A trace of pyridine will cause otherwise stable p-nitrophenylcarbimide to polymerize in dry ether or benzene.<sup>43</sup>

Liquid mixtures of trinitrocresol (m.p. 101°C.) with other nitro compounds when cooled form eutectics as plastic masses.<sup>44</sup> Resinification of a mixture of trinitrocresol and trinitrotoluene occurs when 30-50 per cent of trinitrotoluene is used. When equimolecular proportions of p-nitroaniline and mercaptobenzothiazole are fused, or are heated together in alcoholic solution, a resinous product is formed which has been proposed as a feeble accelerator in rubber vulcanization.<sup>45</sup> For the same purpose, a resinous mixture of di-o-tolylguanidine, 2-mercaptobenzothiazole and phthalic anhydride in stearic acid or acetone solution has been suggested.<sup>46</sup>

Bogert and Stull<sup>47</sup> obtained a yellow gummy material from the interaction of zinc-o-aminoselenophenolate and o-nitrobenzoyl chloride in acetic acid solution, the gum apparently containing zinc in chemical combination.

Considerable resin is formed in the preparation of o-nitrodiphenylarsinic acid from o-nitrodiazobenzene chloride and phenylarsinic oxide in alkaline solution.<sup>48</sup> 10-Ethyl-9-nitroso-9,10-dihydrophenarsazine is described as a thick oil which solidifies to a tough mass. Alkaline solutions of the 10-ethyl and 10-methyl derivatives deposit red resinous masses when allowed to stand.<sup>49</sup> Partial resinification occurs when 2-nitro-6-methyldiphenylamine-6'-arsinic acid is dissolved in alcohol and hydrochloric acid and reduced with sulphur dioxide.<sup>50</sup>

Pernitrosoketocineole when treated with concentrated sulphuric acid at -15°C. yielded a light yellow, unstable solid, C<sub>10</sub>H<sub>14</sub>O (1-acetyl-3-isopropylidene-1-cyclopentene), which was converted into a sticky, brown pitch on exposure to air.<sup>51</sup>

Gummy deposits have been found at times in the mains and meters carrying coke-oven gas or similar gases.<sup>52</sup> Berkhoff<sup>53</sup> has found that such gums contain up to 8 per cent nitrogen and are insoluble in most organic solvents, but soluble in alkali, reprecipitating in acid solution. In the opinion of Berkhoff these resins are polymerization or condensation products of isonitrosites and nitrosates formed by gas-phase reactions between nitrogen peroxide<sup>54</sup> and unsaturated hydrocarbons such as styrene, indene and cyclopentadiene. (See Chapters 5, 9 and 11.)

Investigations of gas-main vapor-phase gum have been made by Jordan, Ward and Fulweiler.<sup>55</sup> The material is described as a dark brown, amorphous powder aggregated into lumps of various sizes. It contains an average of 4-7 per cent nitrogen and 22-32 per cent oxygen. The gum is unstable to heat, decomposing

<sup>42</sup> A. Korczynski, *Gazz. chim. ital.*, 1923, 53 (1), 94; *J.C.S.*, 1923, 124 (1), 560.

<sup>43</sup> C. W. van Hoogstraten, *Rec. trav. chim.*, 1932, 51, 414; *Brit. Chem. Abs. A*, 1932, 597.

<sup>44</sup> N. N. Efremov and A. N. Fikhomirova, *J. Russ. Phys.-Chem. Soc.*, 1927, 59, 373; *Chem. Abs.*, 1928, 22, 2508.

<sup>45</sup> H. M. Bunbury, W. J. S. Naunton and W. A. Sexton, British P. 359,960, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 424.

<sup>46</sup> F. L. Kilbourne, Jr., U. S. P. 1,936,561 and 1,936,562, Nov. 21, 1933, to Firestone Tire & Rubber Co.; *Brit. Chem. Abs. B*, 1934, 394.

<sup>47</sup> M. T. Bogert and A. Stull, *J.A.C.S.*, 1927, 49, 2013.

<sup>48</sup> L. Kalb, *Ann.*, 1921, 423, 59; *Chem. Abs.*, 1921, 15, 2625. E. Sakellarios, *Ber.*, 1924, 57, 1514.

<sup>49</sup> G. A. Rasuvayev, D. A. Godina and T. I. Yemelyanova, *Ber.*, 1923, 63, 606; *Chem. Abs.*, 1923, 26, 2508.

<sup>50</sup> C. S. Gibson and J. D. A. Johnson, *J.C.S.*, 1929, 1254.

<sup>51</sup> A. D'Ambrosio, *Gazz. chim. ital.*, 1927, 57, 717; *Chem. Abs.*, 1928, 22, 774.

<sup>52</sup> See R. L. Brown, *Proc. Am. Gas Assoc.*, 1924, 1353; *Chem. Abs.*, 1925, 19, 2463.

<sup>53</sup> G. Berkhoff, *Het Gas*, 1931, 51, 460; 1932, 52, 119; *Chem. Abs.*, 1932, 26, 1753, 6099.

<sup>54</sup> Nitric oxide and nitrogen peroxide have been detected in such gases by F. Schultze, *Z. anorg. Chem.*, 1929, 42, 787; *Chem. Abs.*, 1929, 23, 4793.

<sup>55</sup> C. W. Jordan, A. L. Ward and W. H. Fulweiler, *Ind. Eng. Chem.*, 1934, 26, 267, 1935. W. H. Fulweiler, *Gas. J.*, 1934, 206, 267; *Brit. Chem. Abs. B*, 1934, 600. See also L. H. Sencide, *ibid.*, 207, 255; *Brit. Chem. Abs. B*, 1934, 812.

violently at 175°C. with the evolution of large quantities of gases. The studies confirmed the observations of Berkhoff that nitrogen peroxide reacts with unsaturated constituents in the gas; and on subsequent polymerization the gum is formed. There was some indication that butadiene and cyclopentadiene (nor-

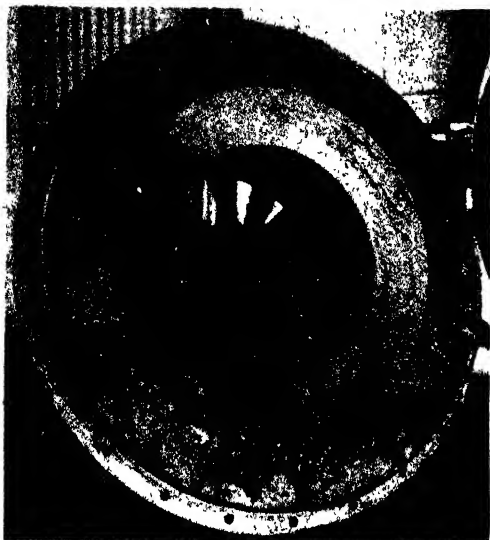


FIG. 118.

Gum Deposit in a Compressor.

Courtesy Industrial and Engineering Chemistry

mally present in the gas) catalyze the oxidation of nitric oxide to nitrogen peroxide.<sup>52</sup>

#### NITRO RESINS FROM PETROLEUM

A nitro resin has been obtained by Edeleanu and Filiti<sup>53</sup> through the nitration of petroleum oil or petroleum distillate (sp. gr. 0.870-0.890). One part of petroleum distillate is run slowly into 3 parts of a well-stirred concentrated acid mixture (5 parts of sulphuric to 1 part of nitric). Unchanged oil is skimmed off and the nitro resin is precipitated by addition of water to the acid solution. It was stated that the product can be used in varnishes and lacquers, as a substitute for camphor in celluloid and as a constituent of explosives when mixed with oxidizing agents. Heating with alkalis converts the resin into a dyestuff.<sup>54</sup> In the writer's laboratory, a dark brown to black resin has been obtained by passing oxides of nitrogen into the highly unsaturated light distillate obtained in the manufacture of Blau gas.

According to Charbonneau,<sup>55</sup> treatment of California petroleum oil with 5-10 per cent of concentrated nitric acid produces various tars and resins. One of them, a brown sticky resin, can be dissolved (1-3 parts) in crude alcohol (100 parts) to form a liquid fuel said to be superior to alcohol alone.

<sup>52</sup> To prevent gum-formation it is suggested that the best method is to remove the nitric oxide. See W. H. Fulweiler, *Gas J.*, 1934, 207, 253; *Chem. Abs.*, 1934, 28, 6277. K. Bunte, *Gas u. Wasserfach*, 1934, 77, 81; *Chem. Abs.*, 1934, 28, 2677. A. L. Ward and C. W. Jordan, U. S. P. 1,976,704, Oct. 9, 1934, to United Gas Improvement Co.; *Chem. Abs.*, 1934, 28, 7441.

<sup>53</sup> L. Edeleanu and G. A. Filiti, U. S. P. 745,802, Dec. 1, 1903. British P. 9416, 1902; *J.S.C.I.*, 1903, 22, 631. French P. 330,618, 1902; *J.S.C.I.*, 1903, 22, 20. German P. 164,064, 1902; *Chem. Zentr.*, 1904, 2, 1177.

<sup>54</sup> L. Edeleanu and G. A. Filiti, German P. 160,428, 1902, addn. to 164,064; *Chem. Zentr.*, 1905, 1, 1189.

<sup>55</sup> E. A. Charbonneau, U. S. P. 1,450,272, Jan. 8, 1924; *Chem. Abs.*, 1924, 18, 825.



One of the few real attempts to use nitro resins was made by Forrest and Meigs.<sup>60</sup> Petroleum distillates, or distillates from native solid bitumens (particularly gilsonite) are nitrated to form resinous products. The distillates from the destructive distillation of gilsonite are best because of their high content of unsaturated material.

Dilute nitric acid (sp. gr. 1.42) is added slowly in small portions while the oil is stirred. Since the reaction is exothermic and quite violent, no more than 1 part of acid to 2500 parts of oil is added at any one time, and the temperature must be kept below 104°C. The reaction is continued until the amount of acid added equals half the amount of oil. The nitro resin is precipitated either by cooling the reaction mixture to 10-24°C. or by running it into cold water. The substance resulting after washing free of acid is light yellow in color, soluble in alcohols and ketones but insoluble in water, dilute mineral acids, petroleum ether and carbon disulphide. The properties of the product vary with the fraction of distillate used. The fraction 65-204°C. produces a viscous oil resembling nitrated castor oil, that from 200-316°C. a light yellow, semi-solid resin, and that from 316-370°C. a hard, solid body. The resins can be mixed with pyroxylin to form lacquers, leather dressings and artificial leather.

Another nitro resin of this type has been made by Day.<sup>61</sup> Powdered gilsonite, grahamite or albertite is dissolved in nitric acid. After the light surface oil has been removed, the acid is diluted with water to precipitate the resin. A solution of the resin in alcohol, ether, benzene or maphtha can be used as a coating composition. A varnish suggested for metals<sup>62</sup> consists of coal tar (75 per cent), benzene (18 per cent) and nitric acid (7 per cent).

Tar has been converted into briquette-binding material in a process devised by Vivian.<sup>63</sup> The tar is heated to about 87°C. and then treated with 5-8 per cent of sulphuric acid and subsequently with 2-3 per cent of nitric acid. When the action of the acids has ceased, paraffin oil is added to reduce the viscosity. The mixture is then cooled, causing the formation of two layers, one consisting of light oils and the other of the heavy binding material. The light oils are removed for subsequent treatment, and the binding-material remaining is freed from acids by washing with water and alkali and is then run into molds to harden. Other uses suggested for the product include the making of road-paving blocks and electrical insulating material.

According to Flexer,<sup>64</sup> a mixture of kerosene and wood tar when nitrated yields a resinous product which can be used in paints and in plastic moldings and can be vulcanized with sulphur to form a rubber substitute. Plastic masses have been made by Reif<sup>65</sup> by mixing fibrous materials with a binder produced by the action of nitric acid on tars and oils.

#### NITROLIGNIN

Fischer and Tropsch<sup>66</sup> prepared nitrolignin by treating 150 g. of lignin<sup>67</sup> with 1 liter of nitric acid (5 N).<sup>68</sup> The solution was first cooled, and then warmed

<sup>60</sup> C. N. Forrest and J. V. Meigs, U. S. P. 1,305,790, June 3, 1919, to Barber Asphalt Paving Co.; *Chem. Abs.*, 1919, 13, 3140. See A. J. Drinberg, A. A. Blagondrayova and E. M. Prik, *J. Appl. Chem. Russ.*, 1934, 7, 1233; *Brit. Chem. Abs.* B, 1935, 319.

<sup>61</sup> D. T. Day, U. S. P. 967,337, Aug. 16, 1910; *Chem. Abs.*, 1910, 4, 3015.

<sup>62</sup> L. Mauerhofer, U. S. P. 1,453,493, June 12, 1923; *Chem. Abs.*, 1923, 17, 2649.

<sup>63</sup> A. W. H. Vivian, *British P.* 210,909, 1923; *Chem. Abs.*, 1924, 18, 1747.

<sup>64</sup> A. S. Flexer, U. S. P. 1,099,976, June 16, 1914; *Chem. Abs.*, 1914, 8, 3301. *British P.* 16,031, 1913; *J.S.C.I.*, 1914, 33, 347. *French P.* 460,230, 1913; *J.S.C.I.*, 1914, 33, 17. *Austrian P.* 6,013, 1913; *Chem. Abs.*, 1913, 7, 1975. *Austrian P.* 74,127, *Kunststoffe*, 1921, 11, 12.

<sup>65</sup> N. Reif, U. S. P. 895,197, Aug. 4, 1908. *German P.* 288,532, 1914, and its addition 290,783, 1915; *Chem. Abs.*, 1916, 10, 2509; 1917, 11, 683. *German P.* 332,941, 1920; *J.S.C.I.*, 1921, 40, 437A.

<sup>66</sup> F. Fischer and H. Tropsch, *Gas. Abhand. Kennst. Kohle*, 1921, 6, 279; *Chem. Abs.*, 1924, 18, 3331. <sup>67</sup> Obtained by the method of R. Willstätter and L. Zechmeister, *Ber.*, 1913, 46, 2406; *J.C.S.*, 1913, 104 (1), 955.

<sup>68</sup> For the action of nitric acid on lignite, coal, humic acids, etc., see W. Eiler, H. Meyer and H. Saenger, *Ann.*, 1923, 431, 163; *Chem. Abs.*, 1923, 17, 2270. E. Donath and F. Braunlich, *Chem.-Ztg.*

until an orange color appeared. Subsequent filtration, washing and air-drying produced the nitrolignin as a soft, yellow powder (60 per cent yield). Analysis indicated the composition  $C_{20}H_{17}O_{10}N_3$  (containing 3 methoxyl and 6 hydroxyl groups). Attempts to reduce nitrolignin with tin and hydrochloric acid resulted in extensive polymerization, yielding a brown amorphous product insoluble in most solvents.

#### NITRATION OF NATURAL RESINS

Resinous material for use in varnishes has been obtained by Fry<sup>66</sup> by nitrating rosin or oil of turpentine. The resins have been termed "Oxycolophones" and "Oxyturpentines," since they are actually oxidation products formed in the process by decomposition of the nitrated substances. Notwithstanding this fact, the resins are mentioned in this chapter because, primarily, the procedure involves nitration.

Nitric acid (10-30 parts, sp. gr. 1.42) is added slowly to powdered rosin (100 parts), the mixture being kneaded to facilitate the reaction and to avoid the formation of lumps. Impure nitrocolophony, an olive-green powder, is obtained by this treatment. Decomposition of the nitrocolophony is accomplished by fusing it in a porcelain container heated by boiling water, resulting finally in a yellow resin. In the nitration and decomposition stages care must be taken because of the explosive character of the nitrocolophony. It is not advisable to work with large batches, since the reaction is exothermic.

Venice turpentine, or a mixture of oil of turpentine (1 part) and rosin (2 parts), is nitrated similarly to form resins. If a soft resin is desired, 10 parts of nitric acid are used for each 100 parts of the turpentine mixture, whereas 30-35 parts of nitric acid are used if a hard product is to be formed. The soft resin is superior to the hard variety in solubility in boiled oil or in oil of turpentine.

Rosin is more easily nitrated than Venice turpentine and the latter more easily than oil of turpentine. Consequently, in the nitration of rosin-turpentine mixtures, the nature of the final product is affected by the time of reaction. To restrict the nitration chiefly to the rosin, the acid is allowed to act only two hours. In this short time the oil of turpentine is not greatly attacked, several days of treatment being required to convert it into a satisfactory resin. The nitration of a solution of rosin in a drying oil produces an alcohol-soluble resin. By heating "Oxycolophones" for several hours at 100-204°C. orange or red tints are developed, making bases for staining-varnishes.

Nitrated colophony has been used directly in varnishes,<sup>67</sup> and other nitrated resins either alone or with oils have been employed in varnishes containing cellulose esters and bitumens.<sup>68</sup> Other suggested uses for nitrated resins of this type include the making of dyestuffs<sup>69</sup> and fixatives for printing inks.<sup>70</sup> The fact that rosin is sometimes selectively nitrated has been used by Donath to detect its presence as an adulterant.<sup>71</sup>

1904, 28, 180; 1912, 36, 373; J.C.S., 1912, 102 (1), 337. J. Marcusson, *Chem.-Ztg.*, 1918, 42, 437; *Z. angew. Chem.*, 1919, 32, 118; 1921, 34, 521; *Chem. Abs.*, 1919, 13, 2592, 2750; 1923, 16, 1496. F. Fischer and H. Schrader, *Brennst. Chem.*, 1921, 2, 313; *Chem. Abs.*, 1921, 15, 2848. H. Tropach and A. Schellenberg, *Ges. Abhand. Kennt. Kohle*, 1921, 6, 191, 257; *Chem. Abs.*, 1924, 18, 2572. F. Fischer and U. Ehrhardt, *Ges. Abhand. Kennt. Kohle*, 1919, 4, 279.

<sup>66</sup> G. Fry, U. S. P. 754,393, Mar. 8, 1904; J.S.C.I., 1904, 23, 378. British P. 19,626, 1903; J.S.C.I., 1906, 22, 972.

<sup>67</sup> J. J. Kessler, U. S. P. 922,596, May 25, 1909; *Chem. Abs.*, 1909, 3, 3063. I. R. Morosov, Russian P. 21,709, 1923; *Chem. Abs.*, 1924, 28, 3006.

<sup>68</sup> J. F. Bennett and J. Hadfield, British P. 231,377, 1926; *Chem. Abs.*, 1926, 22, 3543. N. S. Kocher, U. S. P. 1,973,409, Sept. 11, 1934, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 7043.

<sup>69</sup> E. Arnot, U. S. P. 1,414,184, April 25, 1923, and 1,500,915, July 8, 1924. British P. 173,254, 1926; *Chem. Abs.*, 1923, 16, 1809, 2220; 1924, 18, 2514.

<sup>70</sup> L. Magnien, British P. 379,004, 1931, to Soc. anon. Chlorosoda; *Brit. Chem. Abs. B*, 1932, 997.

<sup>71</sup> H. Donath, *Dingler's polytech. J.*, 1873, 265, 181; J.C.S., 1873, 26, 194. *Chem.-Ztg.*, 1930, 54, 687; *Chem. Abs.*, 1930, 24, 5512.

## NITRO-RESINIC ACIDS

One of the principal constituents of rosin is abietic acid. (See Chapter 37.) In various investigations on the constitution of this acid, nitro derivatives have been formed.<sup>70</sup> In following up the work of earlier investigators, Dubourg<sup>71</sup> obtained crystalline di- and trinitro derivatives, and in addition some resinous products. Abietic acid (20 g.) in an inert solvent, e.g., carbon tetrachloride (200 cc.), when treated with concentrated nitric acid (100 cc.) yielded a yellow-gray, viscous mass. An explosive, amorphous body was produced when water was added to a solution of abietic acid in concentrated nitric acid.

In further studies of the action of nitric acid on abietic acid<sup>72</sup> there were obtained two principal products, one a crystalline dinitro derivative, and the other a yellow, amorphous mass containing nitrogen (decomposes above 100°C.). The yellow mass was found to be readily soluble in alkalies, the solutions absorbing oxygen avidly from the air. Attempts to esterify the sodium salt with alkyl sulphates yielded tarry material.

Amorphous or resinous substances containing nitrogen have been obtained by the action of nitric acid on other resinic acids such as  $\alpha$ -elemic acid,<sup>73</sup>  $C_{27}H_{44}O_6$  (from *Canarium commune*), copal acid,<sup>74</sup>  $C_{28}H_{46}O_6$  (from Congo copal), and tsugic acid,<sup>75</sup>  $C_{18}H_{22}O_7$  (from *Tsuga sieboldii*, Carr).

## RESINS FROM ALIPHATIC NITROGEN COMPOUNDS

Certain of the cyanamides have yielded resinous products in various investigations. For instance acetyl cyanamide and isovaleryl cyanamide have been described as syrup-like compounds which explode when heated, forming amorphous solids.<sup>76</sup> Madelung and Kern<sup>77</sup> found that dicyanamide very readily forms an amorphous polymer of high molecular weight. It is, of course, well known that cyanogen compounds yield cyclic trimers and that cyanogen itself will polymerize. Likewise, hydrogen cyanide forms a trimer in alkaline solution,<sup>78</sup> the reaction producing at the same time a brown, humus-like body, known as azulmic acid,  $C_4H_2N_4O$ . The simple ketene imines,  $H_2C=C=N-R$ , e.g., ketene ethylimine, being very unsaturated, polymerize rapidly at room temperature.<sup>79</sup> It is reported that on long standing  $\alpha,\alpha'$ -tetraethyldiaminoadipic acid solidifies to a glassy hygroscopic material.<sup>80</sup>

In their work on the tetraethylammonium radical, Schlubach and Ballauf<sup>81</sup> obtained a deep blue solution by the electrolysis of tetraethylammonium iodide. It was found that the addition of 2,6-dimethyl-1,4-pyrrone to the solution colored it yellow, and on subsequent evaporation a brown, resinous mass was formed. The electrolysis of potassium alkyl amidines in liquid ammonia to synthesize hydrocarbons has been found to result in resinous deposits on the anode.<sup>82</sup>

<sup>70</sup> T. H. Easterfield and G. Bagley, *J.C.S.*, 1904, 85, 1238. D. Johansson, *Arkiv. Kemi. Min. Geol.*, 1917, 6 (19); *Chem. Abs.*, 1918, 12, 533. A. I. Virtanen, *Ann.*, 1921, 424, 150; *Chem. Abs.*, 1921, 15, 3198.

<sup>71</sup> J. Dubourg, *Bull. inst. pin.*, 1937 (1), 41, 241; *Chem. Abs.*, 1938, 22, 593.

<sup>72</sup> L. A. Goldblatt, A. Lowy and W. B. Burnett, *J.A.C.S.*, 1930, 52, 3132.

<sup>73</sup> H. Lieb and D. Schwarzl, *Monatsh.*, 1924, 45, 81; *J.C.S.*, 1924, 126 (1), 1312.

<sup>74</sup> K. H. Bauer and K. Gonsor, *Chem. Umschau Fette, Öle, Wachse, Harze*, 1930, 33, 230; *Chem. Abs.*, 1927, 21, 2303.

<sup>75</sup> J. Kawamura, *Bull. Imp. Forestry Expt. Sta. Tokyo*, 1933, 31, 73; *Chem. Abs.*, 1933, 26, 4339.

<sup>76</sup> O. Martens, *J. prakt. Chem.*, 1873, 17, 4, 34; *J.C.S.*, 1873, 34, 396.

<sup>77</sup> W. Madelung and E. Kern, *Ann.*, 1928, 427, 1; *J.C.S.*, 1928, 122 (1), 430.

<sup>78</sup> W. Wippmann, *Ber.*, 1874, 7, 767; *J.C.S.*, 1874, 27, 1084.

<sup>79</sup> H. Staudinger and E. Hauser, *Helv. Chim. Acta*, 1921, 4, 537; *Chem. Abs.*, 1922, 16, 1677.

<sup>80</sup> J. von Braun, W. Leistner and W. Münch, *Ber.*, 1906, 39, 1950; *Chem. Abs.*, 1927, 21, 40.

<sup>81</sup> H. E. Schlubach and F. Ballauf, *Ber.*, 1921, 54, 2611; *Chem. Abs.*, 1922, 16, 1391.

<sup>82</sup> E. A. Fulton and F. W. Bergstrom, *J.A.C.S.*, 1934, 56, 167.

Fusion of such proteins as casein, fibrin, elastin and keratin with phthalic anhydride at 200°C. has yielded amorphous products of high molecular weight.<sup>98</sup> A hard and semi-transparent body results from the reaction of soya-bean protein (extracted with methyl alcohol) with formaldehyde.<sup>99</sup> Adhesive and plastic products are obtained by the action of acetaldehyde on casein.<sup>100</sup> A transparent, colloidal mass resistant to solvent action has been obtained by condensing the gases evolved when gelatin (3 parts) is heated with wood creosote (4 parts) at 160-250°C. The material is recommended as a preservative composition for paintings.<sup>91</sup>

#### RESINS FROM AROMATIC AMINES

Aniline when mixed with water and exposed to strong sunlight produces resinous substances soluble in sulphuric acid. This effect is attributed to the development of oxidation products intermediate between aniline and nitrobenzene.<sup>92</sup> In the electrochemical oxidation of asym-m-xyldine to hydroxyxylolquinone, the use of a platinum anode instead of a litharge one leads to the formation of much resinous matter.<sup>93</sup>

König and Buchheim<sup>94</sup> report that the condensation of o-toluidine with bromo- or chloroacetal formed a liquid (b.p. 225-230°C.) which on treatment with nitrous acid yielded small amounts of easily resinifying bodies. Methylene diphenyldiamine and phenol yield a semi-solid resin when heated together in nearly equal proportions.<sup>95</sup> The addition of paraformaldehyde (7-10 per cent) hardens the material somewhat. One of the uses suggested for the resin is the impregnation of brake linings; in this case it is baked into the lining material at 400°C. The condensation of resorcinol with 2,7-N-diacetyldiaminodiphenic anhydride, using zinc chloride at 110°C., is reported to form a red glassy mass.<sup>96</sup>

Alkylene or arylene diamines when heated with naphthols yield naphthalene-substituted diamines, useful as antioxidants in rubber.<sup>97</sup> Thus, for example,  $\beta$ -naphthol reacts with ethylenediamine or with m-phenylenediamine. This is but one example of the many instances of the employment of weak bases as antioxidants for rubber. For this purpose resins prepared by condensing a polyhydroxy aliphatic amino compound (e.g., triethanolamine) with a substance containing an imino grouping, e.g., phenyl- $\alpha$ -naphthylamine have been utilized.<sup>98</sup>

Resinous material is obtained when diphenylamine is heated with d-glutamic acid at 240°C.<sup>99</sup> Also in the manufacture of diphenylamine, tarry compounds are formed.<sup>100</sup> The distillation of 2-2'-diaminodiphenylbutane with hydrochloric or sulphuric acid results in a 40 per cent yield of p-isobutenylaniline. The latter compound after standing 4 days and then being heated for 1 day at 100°C. was converted (25 per cent yield) into a dark-red hard glass.<sup>101</sup>

<sup>98</sup> P. Brigl and E. Klenk, *Z. physiol. Chem.*, 1923, 131, 66; *Chem. Abs.*, 1924, 18, 2501.

<sup>99</sup> T. Hinuma and M. Mashino, *J. Soc. Chem. Ind. Japan*, 1933, 36, 465B; *Brit. Chem. Abs. B*, 1933, 879.

<sup>96</sup> R. Bauer and G. Mauthe, German P. 574,841, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 23, 1485.

<sup>94</sup> H. Deitchman, U. S. P. 1,937,813, Dec. 5, 1933; *Chem. Abs.*, 1924, 23, 1156.

<sup>95</sup> H. Kuns-Krause and P. Manicks, *Ber. pharm. Ges.*, 1923, 32, 232; *Chem. Abs.*, 1923, 17, 901.

<sup>96</sup> F. Fichter and P. Müller, *Helv. Chim. Acta*, 1925, 8, 290; *Chem. Abs.*, 1925, 19, 2192.

<sup>97</sup> W. König and R. Buchheim, *Ber.*, 1925, 58, 2368; *Chem. Abs.*, 1926, 20, 1635.

<sup>98</sup> W. Achtmeyer, U. S. P. 1,429,267, Sept. 19, 1923, and 1,418,607, June 6, 1922; *Chem. Abs.*, 1922, 16, 2761, 4023. Canadian P. 237,679, 1924; *Chem. Abs.*, 1924, 18, 1037.

<sup>99</sup> H. Adkins, E. F. Steinbring and E. Pickering, *J.A.C.S.*, 1924, 46, 1917. Cf. F. Bischoff and H. Adkins, *ibid.*, 1923, 45, 1630.

<sup>100</sup> A. M. Clifford, U. S. P. 1,694,529, Dec. 11, 1923, to Goodyear Tire & Rubber Co. British P. 296,396, 1927. Canadian P. 285,541, 1923; *Chem. Abs.*, 1929, 23, 731, 1012, 2603.

<sup>101</sup> D. F. Twiss and F. A. Jones, British P. 389,637, 1933, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 9032.

<sup>92</sup> W. H. Gray, *J.C.S.*, 1922, 1264.

<sup>93</sup> L. Desvergues, *Chimie et Industrie*, 1923, 23, 759; *Chem. Abs.*, 1923, 27, 964.

<sup>94</sup> J. von Braun, E. Anton, W. Haasael and G. Werner, *Ann.*, 1929, 472, 1; *Chem. Abs.*, 1929, 23, 4668.

Heating dianilinothiourea,  $C_6H_5-NH-NH-CS-NH-NH-C_6H_5$ , with hydrochloric acid for 30 minutes at  $30^\circ C$ . and then for 1 hour at  $60-65^\circ C$ . out of contact with air, yielded diaminodiphenylthiourea,  $NH_2-C_6H_4-NH-CS-NH-C_6H_4-NH_2$ . Black, tarry products resulted in attempts to isolate the free base or its hydrochloride, disulphide or metallic derivatives.<sup>102</sup>

Bromination of phenylisoamylthiocarbamide in chloroform solution gives an orange-red resin. Similar treatment of sym-phenylisobutylthiocarbamide results in a red gum which becomes crystalline on standing and resinous when in contact with diethyl ether or petroleum ether.<sup>103</sup>

The pyrolysis of allylaniline, diallylaniline and diallyl-p-phenetidine at  $275-300^\circ C$ . yielded in each case the parent primary amine, gaseous hydrocarbons (mainly propylene) and considerable resinous material.<sup>104</sup> If 1-phenyl-4-anilino-butadiene is distilled, a red, rosin-like solid is formed.<sup>105</sup> The main product of the thermal decomposition of malonanilide,  $CH_3(CONHC_6H_5)_2$ , is a dark brown, brittle mass.<sup>106</sup> This same resinous material results when aniline and ethyl malonate are heated together. Dark red to brown-black resins are developed on warming  $\beta$ -2,4-dinitrophenylhydroxylamine or its benzoate or acetate.<sup>107</sup>

Vorländer and co-workers<sup>108</sup> have found that the acetyl derivative of tri-p-aminotriphenylacetoneitrile and the condensation product of the latter with anisaldehyde are both amorphous substances. When phenylmethylacetoneitrile is added to a mixture of sodium ethoxide solution and ethyl cyanoacetate, there is formed ethyl  $\alpha$ -cyano- $\beta$ -imino- $\alpha$ -phenylvalerate. This compound, when treated with sulphuric acid, yields ethyl 2,4-diamino-1-methylnaphthalene-3-carboxylate, which changes very readily into a black, resinous mass.<sup>109</sup>

Scheibler and Baumgarten<sup>110</sup> report that ethyl N- $\alpha$ -cyanopiperonylaminoacetate,  $CH_3O_2C=C_6H_4-CH(CN)-NH-CH_2-CO_2C_2H_5$ , is a viscous liquid, which may be converted by the action of alcoholic potash into 3,4-methylenedioxybenzylideneglycine, a pale brown, viscous syrup which solidifies to a glass-like resin. In the benzoylation of trans-phenylserine,  $C_6H_5-CHOH-CHNH_2-COOH$ , there resulted a small amount of a colorless by-product, which when heated at  $160^\circ C$ . was changed into a yellow resin.<sup>111</sup>

#### DIAZONIUM RESINS

The aromatic diazo compounds contain the group  $-N=N-$ . They are of interest because of their great activity and because they constitute the starting point in the preparation of many dyestuffs. The reactivity of these compounds has often led to the formation of resinous material.

The instability of diazonium hydroxides in aqueous solutions was noted by Hantzsch,<sup>112</sup> who found that, even in the cold, decomposition takes place with the formation of a large amount of diazo resin. This reaction was studied further by Angeli and Jolles.<sup>113</sup> Aniline was diazotized in the usual manner and then the solution was made alkaline with potassium hydroxide and allowed to stand

<sup>102</sup> P. C. Guha and H. K. Banerjee, *J. Indian Inst. Sci.*, 1928, 11A, 231; *Chem. Abs.*, 1929, 23, 2187.

<sup>103</sup> R. F. Hunter, *J.C.S.*, 1926, 2056.

<sup>104</sup> F. L. Carnahan and C. D. Hurd, *J.A.C.S.*, 1930, 52, 4586.

<sup>105</sup> I. E. Muskat and L. B. Grimsley, *J.A.C.S.*, 1933, 55, 3765.

<sup>106</sup> P. Baumgarten and W. Kargel, *Ber.*, 1927, 60, 840; *Chem. Abs.*, 1927, 21, 1966.

<sup>107</sup> W. Borsche, *Ber.*, 1923, 56, 1491; *Chem. Abs.*, 1923, 17, 3334.

<sup>108</sup> D. Vorländer and others, *Ber.*, 1925, 58, 1963; *J.C.S.*, 1925, 128 (1), 1256.

<sup>109</sup> H. W. Thompson, *J.C.S.*, 1923, 1330.

<sup>110</sup> H. Scheibler and P. Baumgarten, *Ber.*, 1922, 55, 1353; *J.C.S.*, 1922, 122 (1), 655.

<sup>111</sup> M. O. Forster and K. A. Rao, *J.C.S.*, 1926, 1950.

<sup>112</sup> A. Hantzsch, *Ber.*, 1898, 31, 340; *J.C.S.*, 1898, 74 (1), 307.

<sup>113</sup> A. Angeli and E. Jolles (with W. Camiglietti), *Gazz. chim. ital.*, 1931, 61, 397; *Chem. Abs.*, 1932,

for 7 days until no more nitrogen was evolved. The principal reaction product was a diazo resin (70 per cent yield).

The work was continued by Jolles,<sup>124</sup> studies being made on the resinifying action of alkaline solutions of the diazonium compounds of aniline, o- and p-anisidine, m- and p-toluidine, p-phenetidine, o- and p-aminobenzoic acid and  $\alpha$ -naphthylamine, by allowing their solutions in alkali to stand. Yields of 70-93 per cent were obtained together with traces of the corresponding hydrocarbons. It was supposed that the resinification is caused by the oxidation of one diazotate by another. From the nitrogen content of the resin, Jolles suggested that the diazotized aniline reacts as follows:



The presence of the  $-N=N-$  grouping in the resin is assumed from the fact that aniline is formed when the resin is reduced with tin and hydrochloric acid; and when the resin is oxidized one of the products is benzoic acid. Resins identical with that from diazotized aniline are obtained from phenylazoxycarboxamide and from nitrosoacetanilide on prolonged treatment with alkali.

Hellerman and co-workers<sup>125</sup> have found that  $\beta,\beta'$ -diphenyldiazoethane,  $(C_6H_5)_2CHCH(N_2)$ , can be kept below  $-10^\circ C$ . for several hours without decomposition, but at  $0^\circ C$ . or higher it loses some of its nitrogen and changes to a yellow, resinous mass.

The diazotization of p-nitroaniline sometimes produces resinous substances. For instance, gummy materials have been formed in certain cases when nitrogen tetroxide was used as the diazotizing agent.<sup>126</sup> A considerable amount of a brown resin was obtained when p-nitroaniline was diazotized and then coupled with isosafrole.<sup>127</sup>

Busch and Schöffner<sup>128</sup> found that when aniline is diazotized in hydrochloric acid solution, rendered alkaline and poured into an aqueous solution of potassium nitromethane, a brown-red resinous mass is precipitated, a further quantity being thrown down from the supernatant liquid by carbon dioxide.

Attempts made by Bischler and Brodsky<sup>129</sup> to reduce p-nitrobenzenediazonium chloride to p-nitrophenylhydrazine, using stannous chloride, yielded resinous material. Purgotti<sup>130</sup> tried to accomplish this same reduction using sodium bisulphite. Although some p-nitrophenylhydrazine was formed, the major product was a resinous mass. The experiments of Purgotti were repeated and confirmed by Davies.<sup>131</sup> It was found that the resin formation can be prevented almost completely by using sodium sulphite in neutral or alkaline solution, giving a good yield (80 per cent) of p-nitrophenylhydrazine. If the solution is allowed to acidify, there is obtained an orange-red precipitate of sodium p-nitrodiazobenzene sulphonate, which readily decomposes to form a resin.

In converting 5-aminosalicylic acid into the corresponding thiocyanogen derivative by use of the Sandmeyer reaction, resinification occurs when a temperature higher than  $65^\circ C$ . is employed.<sup>132</sup> The pyrolysis of diazoamino-p-toluene at  $150-170^\circ C$ . yields considerable resinous material of a basic nature.<sup>133</sup> Methyl and ethyl p-azoxycinnamate yield on hydrolysis p-azoxycinnamic acid as a yellow,

<sup>124</sup> Z. Jolles, *Atti. accad. Lincei*, 1903, (5) 15, 292, 395; *Chem. Abs.*, 1923, 26, 5924; *Brit. Chem. Abs. A*, 1923, 541, 943. Cf. E. Bamberger and O. Baudisch, *Ber.*, 1909, 42, 3465; *J.C.S.*, 1909, 96 (1), 977.

<sup>125</sup> L. Hellerman, M. L. Cohen and R. E. Hoen, *J.A.C.S.*, 1923, 50, 1737.

<sup>126</sup> B. Houston and T. R. Johnson, *J.A.C.S.*, 1925, 47, 3017.

<sup>127</sup> A. Quilico and M. Frati, *Gazz. chim. Ital.*, 1923, 53, 330; *Chem. Abs.*, 1923, 23, 597.

<sup>128</sup> M. Busch and S. Schöffner, *Ber.*, 1923, 56, 1612; *Chem. Abs.*, 1924, 18, 48.

<sup>129</sup> A. Bischler and S. Brodsky, *Ber.*, 1899, 22, 2615.

<sup>130</sup> A. Purgotti, *Atti. accad. Lincei*, 1901, 2, 269; *Ber.*, 1892, 25, 119R.

<sup>131</sup> W. Davies, *J.C.S.*, 1923, 121, 715.

<sup>132</sup> H. P. Kaufmann and E. Rosbach, *Ber.*, 1926, 59, 1596; *Chem. Abs.*, 1926, 20, 123.

<sup>133</sup> G. T. Morgan and L. F. Walls, *J.C.S.*, 1926, 1505.

amorphous solid insoluble in the common organic solvents but soluble in alkali.<sup>124</sup>

#### RESINS FROM HYDRAZINE AND RELATED SUBSTANCES

The hydrazines, hydrazones, alkazines and hydrazides are to be considered together because of their similarity in structure, all of them having the =N—N= linkage.

The addition of phenylhydrazine to an alcoholic solution of chloroacetophenone mixed with an aqueous solution of sodium acetate produced a resinous mass when the mixture was heated to 40°C. and stirred.<sup>125</sup> Similarly resinous products have been obtained from a mixture of phenylhydrazine and 2-ethyl-1-hydrindone heated at 130°C. for 7 hours.<sup>126</sup> In studies of the action of cyclohexyl bromide on arylhydrazines it was found that the reaction of  $\alpha$ -naphthylhydrazine with cyclohexylbromide resulted in resin formation.<sup>127</sup> Dimethylpyrone reacts with hydrazine hydrate to form a viscous, almost colorless liquid. Heated at 240°C. under 10 mm. pressure, the liquid becomes a faint-yellow glass-like mass. On further heating, ammonia is split off and a hard, bright-yellow substance,  $C_{14}H_{17}N_8$ , results.<sup>128</sup>

A semi-transparent gel is formed by heating anhydrous hydrazine with cellulose in a closed bomb tube. On opening the tube, ammonia is evolved and the residue turns to a green glassy substance as it is dried over sulphuric acid.<sup>129</sup>

It was noted by Ottolino<sup>130</sup> that the interaction of phenylhydrazine hydrochloride (2 mols) and benzaldehyde (3 mols) produces a dark green, friable resin (40 per cent yield). When the condensation is carried out in the presence of arsenic acid, the resin is harder and a higher yield is obtained (60 per cent).

Previous experiments by Ciusa and Ottolino<sup>131</sup> showed that this resin also results on heating zinc chloride with phenylhydrazine and benzaldehyde. The suggested formula for the product is



In these experiments an intense green resin of the same type was formed by the action of dry hydrogen chloride or of hot concentrated hydrochloric acid on hot alcoholic solutions of aromatic arylhydrazones.

The resinifying action of zinc chloride on hydrazones was mentioned by Minunni,<sup>132</sup> who found this tendency was a difficulty to be overcome in his synthesis of pyrazolecarboxylic acids by the interaction of aldehyde hydrazones and acetoacetic ester in the presence of zinc chloride.

Studies on the thermal decomposition of azines, principally aldazines and ketazines, were made by Howard and Hilbert.<sup>133</sup> The pyrolysis of benzaldazine at 290–310°C. yielded as a residue a hard brown resin (82 per cent yield), from which some crystalline substances were obtained by ether extraction. Resinous materials were obtained also in the pyrolysis of anisaldazine, p-tolualdazine, benzophenoneketazine and acetophenoneketazine.

<sup>124</sup> H. B. Nisbet, *J.C.S.*, 1927, 2084.

<sup>125</sup> A. P. J. Hoogveen, *Rec. trav. chim.*, 1931, 50, 669; *Chem. Abs.*, 1931, 25, 4879.

<sup>126</sup> H. Leuchs and G. Kowalski, *Ber.*, 1925, 58, 2826; *Chem. Abs.*, 1926, 20, 1619.

<sup>127</sup> M. Busch and A. Becker, *J. prakt. Chem.*, 1927, (2) 116, 34; *Brit. Chem. Abs. A.*, 1927, 761.

<sup>128</sup> N. Kishner, *J. Russ. Phys.-Chem. Soc.*, 1924, 55, 539; *Chem. Abs.*, 1925, 19, 2622.

<sup>129</sup> E. Müller and H. K. Kraemer-Willenberg, *Ber.*, 1924, 57, 575; *Chem. Abs.*, 1924, 18, 2665.

<sup>130</sup> G. Ottolino, *Gazz. chim. Ital.*, 1923, 53, 227; *Chem. Abs.*, 1923, 26, 4313.

<sup>131</sup> R. Ciusa and G. Ottolino, *Gazz. chim. Ital.*, 1931, 61, 189, 799; *Chem. Abs.*, 1931, 25, 3974; 1932, 26, 1587.

<sup>132</sup> G. Minunni, with G. Lassarini and S. D'Urso, *Gazz. chim. Ital.*, 1925, 55, 502; *Chem. Abs.*, 1926, 20, 606.

<sup>133</sup> L. B. Howard and G. E. Hilbert, *J.A.C.S.*, 1933, 54, 2622.

The hydrazides of aromatic carboxylic acids are usually prepared from the esters of these acids by the action of hydrazine hydrate. Alexa and Gheorghiu<sup>124</sup> found that, with some acid anhydrides, hydrazine hydrate forms dihydrazides, but that in the case of succinic, glutaric and maleic acid anhydrides, non-crystalline gums are developed.

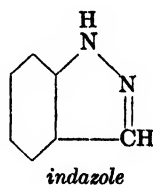
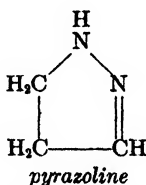
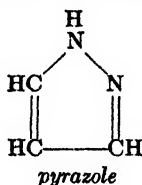
Witte<sup>125</sup> has prepared hydrazides of nitrobenzenesulphonic acids by the action of hydrazine hydrate on the corresponding sulphonyl chlorides. Some of the preparations resulted in crystalline compounds, but in the case of sym-2,2'-dinitro-dibenzenesulphonhydrazide resinous products were formed.

Curtius and Moll<sup>126</sup> report that the dihydrazide of o-carboxyphenoxyacetic acid when heated with methyl, ethyl or benzyl alcohol is converted into an impure diurethan. A resinous product results when the diurethan is hydrolyzed by hydrochloric acid. Resins were obtained by Bertho and Hölder<sup>127</sup> by heating, in ethyl or methyl alcohol, the dihydrazide of 1-p-xylyl-1,2,3-triazole-4,5-dicarboxylic acid.

Oxidation of the dihydrazide of diphenic acid with potassium ferricyanide in ether and ammonium hydroxide yielded the monohydrazide and some resinous aldehydic matter.<sup>128</sup>

### PIRAZOLES AND INDAZOLES

In the pyrazole group are included all compounds with the skeleton ring containing 3 carbon and 2 nitrogen atoms. Pyrazole, pyrazoline and indazole have the following structures:



Indazoles are related to the pyrazoles, their ring system consisting of a condensed benzene-pyrazole nucleus.

One of the methods of preparing pyrazolines consists in reacting unsaturated ketones with hydrazines. Auwers and Kreuder<sup>129</sup> found that 1-phenyl-3-isobutenyl-5,5-dimethylpyrazoline (from phorone and phenylhydrazine) forms a dark brown resin in contact with the air. When 1-nitroso-5-phenylpyrazoline is heated with mineral acids the nitroso group is split off and a resinous product is formed.<sup>140</sup>

Auwers and Strödter<sup>141</sup> found that 3-p-anisylindazole changes to a resinous mass when distilled at 205°C. under 10 mm. pressure. They noted also that the esters of indazole-1-carboxylic acid when heated lose carbon dioxide, forming amorphous products and small amounts of 1- and 2-alkylindazoles. Attempts made to replace the hydroxyl hydrogen of 2-hydroxy-3-phenylindazole by the acetyl, benzoyl or methoxyl group produced resinous substances.<sup>142</sup>

Auwers and Mauss<sup>143</sup> prepared N-methyl-N-benzimidazolium iodide from ben-

<sup>124</sup> V. Alexa and G. Gheorghiu, *Bull. soc. chim.*, 1931, (4) 49, 1112; *Chem. Abs.*, 1932, 26, 720.

<sup>125</sup> A. A. M. Witte, *Rec. trav. chim.*, 1932, 51, 299; *Chem. Abs.*, 1932, 26, 2438.

<sup>126</sup> T. Curtius and K. Moll, *J. prakt. Chem.*, 1930, 123, 106; *Brit. Chem. Abs. A*, 1930, 766.

<sup>127</sup> A. Bertho and F. Hölder, *J. prakt. Chem.*, 1928, 119, 189; *Chem. Abs.*, 1928, 22, 3411.

<sup>128</sup> L. Kalb and O. Gross, *Ber.*, 1926, 59, 727; *Chem. Abs.*, 1926, 20, 2671.

<sup>129</sup> K. von Auwers and A. Kreuder, *Ber.*, 1925, 58, 1952; *Chem. Abs.*, 1926, 20, 761.

<sup>140</sup> K. von Auwers and P. Heimke, *Ann.*, 1927, 458, 180; *Chem. Abs.*, 1928, 22, 421.

<sup>141</sup> K. von Auwers and P. Strödter, *Ber.*, 1926, 59, 829; *Chem. Abs.*, 1926, 20, 2495.

<sup>142</sup> K. von Auwers and K. Hüttenes, *Ber.*, 1925, 58, 1112; *Chem. Abs.*, 1925, 19, 2654.

<sup>143</sup> K. von Auwers and W. Mauss, *Ber.*, 1926, 59, 2416; *Chem. Abs.*, 1926, 22, 1697.

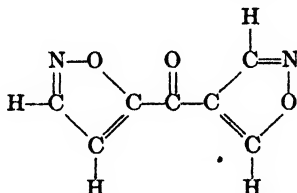


zylimidazol and methyl iodide. The product was converted into a resin when heated at 250-270°C.

#### NITROGEN-CONTAINING ALDEHYDES AND KETONES

The nitro-substituted ketones and aldehydes have been discussed in a previous section of this chapter. Rojahn and Seitz<sup>144</sup> found that the 3- and 5-pyrazolealdehydes are oily liquids resembling aromatic aldehydes in general reactions. However, in the Cannizzaro reaction there are formed only traces of the corresponding carboxylic acids, the major product consisting of resinous bodies.

In experiments conducted by Freri<sup>145</sup> the action of fuming nitric acid on acetylene produced  $\alpha,\beta$ -di-isoxazole ketone to which was assigned the structure



Mixtures of this ketone with benzene and with toluene formed pitchy masses if exposed to sunlight.

The reaction of benzoyl cyanide with resorcinol in cold dry ether, in the presence of zinc chloride and hydrogen chloride, yields a tough, red-brown resin.<sup>146</sup> Boiling acids decompose 4-hydroxy-1-azidoacetylbenzene,  $N_3-CH_2-CO-C_6H_4OH$ , forming green resinous products.<sup>147</sup>

#### RESINS FROM PYRIDINE

Resinous products have been derived from both the reduction and oxidation of pyridine and its derivatives. A considerable amount of resinous matter was obtained in the oxidation of pyridine with dibenzoyl peroxide.<sup>148</sup> Shaw<sup>149</sup> noted that if 95 per cent alcohol is used with sodium in place of absolute alcohol, the reduction of pyridine by Ladenburg's method<sup>150</sup> yields no piperidine, but ammonia is evolved and the main product is a brown, non-nitrogenous resin. The dehydrogenation of pyridine through the agency of anhydrous metallic salts, e.g., ferric chloride<sup>151</sup> or cobaltic chloride,<sup>152</sup> results in the formation of resins.<sup>153</sup>

Emmert and Werb<sup>154</sup> prepared a colorless, crystalline compound, 1,2,4,6-1',2',4',6'-octamethyltetrahydro-4,4'-bipyridyl, by methiodination and subsequent reduction of 2,4,6-trimethylpyridine. It was found that this compound rapidly resinified when exposed to the atmosphere. In alcoholic solution it decolorized iodine with the formation of an amorphous mass. Treatment of diisoamylpyridylum

<sup>144</sup> C. A. Rojahn and A. Seitz, *Ann.*, 1924, 437, 297; *J.C.S.*, 1924, 126 (1), 875.

<sup>145</sup> M. Freri, *Gazz. chim. ital.*, 1933, 63, 419; *Chem. Abs.*, 1933, 27, 5337.

<sup>146</sup> W. Borsche and C. Walter, *Ber.*, 1926, 59, 463; *Chem. Abs.*, 1926, 20, 2323.

<sup>147</sup> K. Fries and K. Saffien, *Ber.*, 1926, 59, 1246; *Chem. Abs.*, 1926, 20, 3004.

<sup>148</sup> J. Overhoff and G. Tilman, *Rec. trav. chim.*, 1929, 48, 993; *Chem. Abs.*, 1929, 23, 5185.

<sup>149</sup> B. D. Shaw, *J.C.S.*, 1924, 125, 1930.

<sup>150</sup> A. Ladenburg, *Ber.*, 1884, 17, 186; *J.C.S.*, 1884, 45, 760.

<sup>151</sup> G. T. Morgan and F. H. Burrell, *J.C.S.*, 1932, 20.

<sup>152</sup> G. T. Morgan and F. H. Burrell, *J. Indian Chem. Soc. P. C. Ray Commemoration Vol.*, 1933, 1; *Chem. Abs.*, 1933, 27, 5330.

<sup>153</sup> See G. T. Morgan, *J.S.C.I.*, 1928, 49, 1227. Resins are amorphous solids of a basic nature. On fusion they become clear and glassy. The resins are insoluble in ether but dissolve in alcohol and in dilute mineral acids. Evaporation of such solutions results in film-formation. See the latter part of Chapter 13.

<sup>154</sup> B. Emmert and O. Werb, *Ber.*, 1923, 56, 1357; *J.C.S.*, 1923, 123, 680.

iodide solution with silver oxide and subsequent hydrogen-reduction of the filtrate at 95°C. leads to the formation of a black resin.<sup>155</sup>

Amorphous products were obtained in the reduction of 2-phenyl-5-benzoylpyridine with amalgamated zinc and hydrochloric acid.<sup>156</sup> It has also been noted that 2-methyl-5-acetylpyridine reacted with ethyl formate and sodium ethylate to form the sodium salt of 2-methyl-5-(hydroxymethyleneacetyl)pyridine. Subsequent treatment of this salt with sulphuric acid and copper sulphate resulted in a yellow oil (presumably the free ketone) which resinsified on exposure to air.

The reduction of 2-methyl-6-phenyleinchomeronic acid (5 g.) with sodium amalgam (75 g., 2.5%) yielded  $\alpha$ -benzoylmethyl- $\gamma$ -valerolactone as an exceedingly viscous oil.<sup>157</sup> When twice as much sodium amalgam was used the product obtained was  $\alpha$ -( $\beta$ -hydroxypropyl)- $\gamma$ -phenyl- $\gamma$ -butyrolactone as a yellow, semi-solid, glassy mass. The barium salt of this acid is glass-like and brittle.

When methyl-2-diphenyl-4,6-pyridinephenylimine is heated in alcoholic solution, rearrangement occurs forming o-aminobenzyl-2-diphenyl-4,6-pyridine.<sup>158</sup> Resinous substances result when this is treated with concentrated hydrochloric acid, and also when treated with methyl iodide.

Scholtz<sup>159</sup> reports that p-xylenedipiperidide reacts with m-xylene bromide in chloroform to give a mixture of  $\alpha$ - and  $\beta$ -m-xylene-p-xylenedipiperidinium dibromides. The same result is obtained when m-xylenedipiperidide reacts with p-xylene bromide. Whereas Scholtz described both bromides as crystalline substances, Meisenheimer and his co-workers<sup>160</sup> in repeating this work found that although the  $\beta$ -bromide is crystalline, the  $\alpha$ -bromide is obtained either as an amorphous powder or as a glassy mass.

Pyrollopyridine derivatives, or indolizines, were prepared by Chichibabin<sup>161</sup> by the reaction between  $\alpha$ -halogen aldehydes and ketones and  $\alpha$ -alkylpyridines. With quinaldine the resulting benzo-indolizines were obtained as resins, presumably polymers of the indolizines. Quinaldine and dibenzoylperoxide reacted to form dibenzoylquinaldine and a resinous substance. Also, the halogen addition product of indolizine was changed to an oily base in potassium hydroxide solution, this oily body oxidizing to a red resin in the air. Le Fevre<sup>162</sup> has obtained gummy products in the reaction of piperidine with 6-nitropiperonal and with 2,7-dibromo-4,6-dinitroxanthene.

Attempts made by Vorländer and his associates<sup>163</sup> to methylate or ethylate p-hydroxyphenylpyridone led to the formation of tars. N-phenyl- $\gamma$ -chloropyridinium chloride (obtained from N-phenylpyridone and thionyl chloride) forms a brown resin in cold sodium hydroxide solution. When p-nitrobenzylpyridinium halides are treated with sodium hypobromite, p-nitrobenzoic acid is obtained. The use of benzylpyridinium halides (without the nitro group) leads to resins practically insoluble in alkali.<sup>164</sup>

Chichibabin<sup>165</sup> noted that the reaction between phenacyl bromide and  $\alpha$ -aminopyridine produced the hydrobromide of 2-phenylpyrimidazole and of another base, N,N'-diphenacyl- $\alpha$ -pyridone imide. The hydrochloride of this latter compound is a colorless, viscous resin. Almost equal weights of phenacyl bromide

<sup>155</sup> B. Emmert and V. Dollein, *Ber.*, 1923, 56, 2068; *Chem. Abs.*, 1924, 18, 689.

<sup>156</sup> E. Benary and H. Psille, *Ber.*, 1924, 57, 828; *Chem. Abs.*, 1924, 18, 2895.

<sup>157</sup> O. Mumm and K. Brodersen, *Ber.*, 1923, 56, 2295; *Chem. Abs.*, 1924, 18, 1128.

<sup>158</sup> W. Schneider and K. Weiss, *Ber.*, 1928, 61, 2449; *Chem. Abs.*, 1929, 23, 1640.

<sup>159</sup> M. Scholtz, *Ber.*, 1911, 44, 480; *Chem. Abs.*, 1911, 5, 1765.

<sup>160</sup> J. Meisenheimer, E. Stratmann and W. Theilacker, *Ber.*, 1932, 65, 418; *Chem. Abs.*, 1932, 26, 2979.

<sup>161</sup> A. E. Chichibabin, *Ber.*, 1927, 60, 1607; *Chem. Abs.*, 1928, 22, 79.

<sup>162</sup> R. J. W. Le Fevre, *J.C.S.*, 1928, 3249.

<sup>163</sup> D. Vorländer (with others), *Ber.*, 1925, 58, 1908; *Chem. Abs.*, 1926, 20, 586.

<sup>164</sup> C. H. Fisher, *J.A.C.S.*, 1924, 56, 2056.

<sup>165</sup> A. E. Chichibabin, *Ber.*, 1926, 59, 2053; *Chem. Abs.*, 1927, 21, 246.

and phenyl pyrimidazole when melted together produce a transparent, nearly colorless resin, easily soluble in water. At 100°C.  $\alpha$ -picoline reacts with alkali iridohexachlorides to form crystalline trichloro-tri- $\alpha$ -picolino-iridite. The reaction at 50°C., however, yields resinous products.<sup>166</sup>

#### RESINS FROM QUINOLINE

The reduction of quinoline with sodium amalgam (25 per cent sodium) yields a small amount of biquinoline and a large amount of a yellow, resinous base.<sup>167</sup> Resinous products were obtained by Conolly<sup>168</sup> from the action of sodium on 6-methylquinoline, 7-methylquinoline and 8-methylquinoline, respectively.

Studies on the Beyer synthesis<sup>169</sup> of quinoline derivatives have been made by Roberts and Turner.<sup>170</sup> Their method consists essentially in the reaction of substituted anilines with a mixture of paraldehyde, acetone and hydrogen chloride in nitrobenzene. Resinous or tarry materials were obtained in attempts to condense the following: 2,4,5-trichloroaniline, p-nitraniline, 3-chloro-6-nitraniline and 3,4-dichloro-6-nitraniline. Tars were also secured in some of the efforts at reduction and diazotization of the quinoline derivatives.

When quinoline is heated at its boiling point with barium oxide there is formed some carbostyryl and a large amount of a dark, thick resin.<sup>171</sup> Condensation of quinoline with epichlorohydrin in sodium hydroxide yields a dark red, semi-oily mass which solidifies in a dry atmosphere.<sup>172</sup> Extraction of this mass with alcohol removes a small amount of a red compound,  $C_{10}H_{12}N_2$ , and leaves resinous material. The action of acetic anhydride on 2-phenyl-4-aminoquinoline also yields a resin-like mass.<sup>173</sup>

The yellow picrate of 1-methyl-2-isobutyl-1,2-dihydroquinoline easily changes into a mixture of resinous material and a red picrate.<sup>174</sup> Considerable resin is also formed in the conversion of 2-isobutylquinoline into its picrate. When 1-methyl-2-phenyl-1,2-dihydroquinoline is heated at 250°C. in an inert atmosphere a resinous polymer is formed.

Resinous products have been obtained from isoquinoline derivatives by Haworth, Perkin and Rankin,<sup>175</sup> by Child and Pyman<sup>176</sup> and by Gulland and Virden.<sup>177</sup>

Certain oxyaminoquinolines used as pharmaceutical products have been described as yellow oils which solidify to glassy masses. Among these are 6-methoxy- and 6-ethoxy-8-aminoquinoline<sup>178</sup> and 8-(2-dimethylaminocyclohexylamino)-6-methoxyquinoline.<sup>179</sup>

The oxidation of p-aminophenol with silver oxide yields quinone monoimine.<sup>180</sup> The quinone imines tend to polymerize, especially in the presence of acids, though the presence of alkyl groups in the nucleus lessens this tendency.<sup>181</sup>

<sup>166</sup> M. Guillot, *Compt. rend.*, 1926, 182, 1090; *Chem. Abs.*, 1926, 20, 2295.

<sup>167</sup> C. G. Williams, *Chem. News*, 1881, 43, 145; *J.C.S.*, 1881, 40, 613.

<sup>168</sup> E. J. V. Conolly, *J.C.S.*, 1925, 127, 2084.

<sup>169</sup> C. Beyer, *J. prakt. Chem.*, 1886, 33, 393; *J.C.S.*, 1886, 50, 629.

<sup>170</sup> E. Roberts and E. E. Turner, *J.C.S.*, 1927, 1832.

<sup>171</sup> A. E. Chichibabin, *Ber.*, 1923, 56, 1879; *Chem. Abs.*, 1924, 18, 394.

<sup>172</sup> M. Gius, *Gazz. chim. ital.*, 1922, 52 (1), 349; *J.C.S.*, 1922, 122 (1), 681.

<sup>173</sup> H. John, *Ber.*, 1926, 59, 1451; *Chem. Abs.*, 1926, 20, 3010.

<sup>174</sup> J. Meisenheimer, E. Stots and K. Bauer, *Ber.*, 1925, 58, 2320; *Chem. Abs.*, 1926, 20, 1081.

<sup>175</sup> R. D. Haworth, W. H. Perkin, Jr. and J. Rankin, *J.C.S.*, 1925, 127, 1445.

<sup>176</sup> R. Child and F. L. Pyman, *J.C.S.*, 1929, 2010.

<sup>177</sup> J. M. Gulland and C. J. Virden, *J.C.S.*, 1929, 1892.

<sup>178</sup> W. Schulemann, F. Schönhöfer and F. Meitzsch, U. S. P. 1,703,365, Feb. 26, 1929, to Winthrop Chemical Co.; *Chem. Abs.*, 1929, 23, 995.

<sup>179</sup> W. Schulemann, F. Schönhöfer and A. Wingler, Canadian P. 284,097, 1928, to Winthrop Chemical Co.; *Chem. Abs.*, 1929, 23, 669.

<sup>180</sup> R. Willstätter and A. Pfannenstiel, *Ber.*, 1904, 37, 4605; *J.C.S.*, 1905, 88 (1), 69.

<sup>181</sup> B. Cordone, *Helv. Chim. Acta*, 1924, 7, 956; *J.C.S.*, 1924, 126 (1), 1335; *Chem. Abs.*, 1925, 19, 981.

## RESINS FROM PYRROLE

Pyrrole,  $C_4H_5N$ , is similar in structure to pyridine but is much less stable. It dissolves slowly in dilute acids but is rapidly resinified in concentrated mineral acids. The addition of alkali to dilute hydrochloric acid solutions of pyrrole and its derivatives does not regenerate the original bases but causes resin formation. The substances obtained are polymers of pyrrole and its derivatives.<sup>182</sup> Although concentrated hydrochloric acid resinifies pyrrole, the introduction of dry hydrogen chloride into an ether solution of pyrrole causes no resinification,<sup>183</sup> but forms the hydrochloride of tripyrrole,  $(C_4H_5N)_3 \cdot HCl$ .

Pyrrole can be converted into tripyrrole by dissolving 25 cc. in 100 cc. of hydrochloric acid (20 per cent), diluting the solution with 500 cc. of cold water and adding ammonia slowly until no more precipitate forms.<sup>184</sup> The tripyrrole is recovered from this amorphous precipitate by ether extraction. This trimer is unstable and is soon transformed into a higher polymer (m.p.  $121^\circ C$ .) which is not soluble in ether. If tripyrrole is heated to  $100^\circ C$ ., ammonia is evolved and a bright brown, glassy mass results. If this mass is further heated to  $300^\circ C$ . it breaks down into indole and pyrrole. Ammonia is also evolved from dilute acid solutions of pyrrole when they are heated, leaving an amorphous, red powder known as pyrrole red.

The analysis of tripyrrole by Tronov and Popov<sup>185</sup> indicates the formula  $C_{12}H_{17}N_3O$ . These workers stated that tripyrrole has never been isolated as the oxygen-free base. In their experiments the action of alkalies or of ammonium hydroxide on the hydrochloride of tripyrrole caused the formation of the pyrrole red,  $C_{12}H_{14}N_3O$ , mentioned above. Tripyrrole has been obtained from pyrrole by the condensing action of ethylene glycol and of glycerol.<sup>186</sup>

The oxidation of pyrrole and its derivatives yields syrupy mixtures which solidify to vitreous masses.<sup>187</sup> Considerable work has been performed by Freri<sup>188</sup> on the oxidation of pyrrole and tripyrrole with ozone. Depending on the conditions and the solvents used, resinous substances of various colors are formed in some cases, and in others the products resemble the pyrrole blacks obtained with other oxidizing agents.

A study of the pyrrole blacks has been made by Quilico,<sup>189</sup> who expressed the belief that all the blacks are formed by the condensation of oxypyrrole nuclei,  $(C_4NO)$ . Although pyrrole blacks are usually formed by oxidation, Illari<sup>190</sup> has obtained a compound of this type by condensation in a strongly reducing medium, through the action of formic acid on pyrrole. Black, amorphous condensation products of high molecular weight result<sup>191</sup> when either  $\alpha$ -dichloro- or  $\alpha$ -trichloroacetylpyrrole is boiled with aqueous potassium hydroxide (5 per cent solution).

Both 4-methyl-2-ethylpyrrole and pyrrole-N-carboxylic acid are unstable. The former resinifies in contact with the air<sup>192</sup> and the latter in dilute mineral acids.<sup>193</sup>

<sup>182</sup> G. Ciamician and C. M. Zanetti, *Ber.*, 1893, 26, 1711; *J.C.S.*, 1893, 64 (1), 602.

<sup>183</sup> M. Dennstedt and J. Zimmermann, *Ber.*, 1888, 21, 1478.

<sup>184</sup> M. Dennstedt and F. Voigtländer, *Ber.*, 1894, 27, 476; *J.C.S.*, 1894, 66 (1), 259.

<sup>185</sup> B. V. Tronov and P. P. Popov, *J. Russ. Phys.-Chem. Soc.*, 1926, 58, 745; *Chem. Abs.*, 1927, 21, 3619.

<sup>186</sup> A. K. Plisov, *Ukrain. Khim. Zhur.*, 1928, 3 (Sci.), 471, 477; *Chem. Abs.*, 1929, 23, 3223, 3224.

<sup>187</sup> A. Pieroni and P. Veremeenco, *Gazz. chim. ital.*, 1926, 56, 455; *Chem. Abs.*, 1927, 21, 248.

<sup>188</sup> M. Freri, *Gazz. chim. ital.*, 1932, 62, 600; 1933, 63, 281; *Chem. Abs.*, 1933, 27, 85, 4795.

<sup>189</sup> A. Quilico, *Gazz. chim. ital.*, 1932, 62, 882; *Chem. Abs.*, 1933, 27, 504.

<sup>190</sup> G. Illari, *Gazz. chim. ital.*, 1933, 63, 591; *Chem. Abs.*, 1934, 28, 1842.

<sup>191</sup> G. Sanna and F. Athene, *Gazz. chim. ital.*, 1933, 63, 479; *Chem. Abs.*, 1934, 28, 763.

<sup>192</sup> H. Fischer and J. Klarer, *Ann.*, 1926, 447, 48; *Brit. Chem. Abs. A*, 1926, 412.

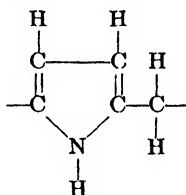
<sup>193</sup> W. Chelintsev and B. Mazorov, *Ber.*, 1927, 60, 197; *Chem. Abs.*, 1927, 21, 1648.

Feist<sup>194</sup> found from his experiments that pyrrole derivatives with more than 1 hydrogen atom in the ring will combine with aromatic aldehydes in molecular proportions. In most of the reactions of this type crystalline compounds were obtained, although resinous masses were formed in the reaction of 2,4-dimethylpyrrole with benzaldehyde and with p-nitrobenzaldehyde and of the ethyl ester of 4,6-dimethylpyrrole-3-carboxylic acid with cinnamic aldehyde and with salicylic aldehyde.

If acetaldehyde and pyrrole are heated together in a sealed tube the mixture is converted into a dark brown gum, perhaps a product of polymerization.<sup>195</sup> Tars are formed when pyrrole is condensed with some ketones such as methylethyl and phenylethyl ketones and 1- and 2-methylcyclohexanones.<sup>196</sup> Resins applicable in photography are formed by the reaction of five-membered mono-heterocyclic compounds (e.g., pyrrole) with methylethyl ketone, aniline or  $\alpha$ -naphthylamine.<sup>197</sup>

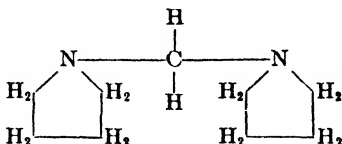
Pictet and Rilliet<sup>198</sup> noted that formaldehyde (40 per cent) and pyrrole react readily, yielding an insoluble, hard, red mass. If 4 per cent formaldehyde is used there is formed formaldehydopyrrole,  $C_4H_5ON_2$ , a white, insoluble compound which will not crystallize.

It was observed by Chelintzev and Maksorov<sup>199</sup> that pyrrole and formaldehyde (4 per cent), condensed with hydrochloric or sulphuric acid as a catalyst yield an amorphous, rose-colored polymer (m.p. 82-83°C.) containing a residue comprised of 6 to 8 of the following groupings:



When this polymer is heated to 140°C. and then cooled it forms a transparent, vitreous body.

Equimolecular proportions of pyrrolidine and formaldehyde (as trioxymethylene) when heated together in sealed tubes for 6 hours at 145-150°C. yield a homogeneous amorphous mass.<sup>200</sup> If this mass is dried with potassium hydroxide and distilled (at 30 mm.) a dark resinous residue is obtained. From the distillate two liquids, pyrrolidinomethyl alcohol and N,N'-dipyrrolidinomethane,



are recovered, the latter possessing a strong tendency to resinify.

<sup>194</sup> F. Feist, *Ber.*, 1902, 35, 1647; *J.C.S.*, 1902, 82 (1), 490. See also U. Colacicchi and C. Bertoni, *Atti. accad. Lincei*, 1912, (5) 21 (1), 600; *J.C.S.*, 1912, 102 (1), 653.

<sup>195</sup> A. K. Plisov, *loc. cit.*

<sup>196</sup> B. V. Tronov and P. P. Popov, *J. Russ. Phys.-Chem. Soc.*, 1927, 59, 327; *Chem. Abs.*, 1928, 22, 2561. See also V. V. Chelintzev and B. V. Tronov, *J. Russ. Phys.-Chem. Soc.*, 1916, 48, 105; *Chem. Abs.*, 1917, 11, 452.

<sup>197</sup> M. C. Beebe, A. Murray and H. V. Herlinger, U. S. P. 1,537,269, June 1, 1926, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1926, 20, 2292. See the last sections of Chapters 21 and 24.

<sup>198</sup> A. Pictet and A. Rilliet, *Ber.*, 1907, 40, 1166; *Chem. Abs.*, 1907, 1, 1569.

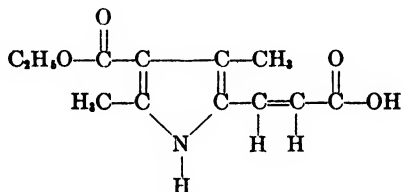
<sup>199</sup> V. V. Chelintzev and B. V. Maksorov, *J. Russ. Phys.-Chem. Soc.*, 1916, 48, 748; *Chem. Abs.*, 1917, 11, 752.

<sup>200</sup> N. J. Putochin, *Ber.*, 1922, 55, 2749; *Chem. Abs.*, 1923, 17, 1016.

If gaseous formaldehyde is passed into magnesylpyrrole in ether, and the mixture then heated on the water bath for 2 hours and subsequently decomposed with ice-cold aqueous ammonium chloride, resinous products are obtained.<sup>301</sup> Magnesylpyrrole, sulphur and benzoyl chloride have been found to form a black infusible, insoluble substance.<sup>302</sup>

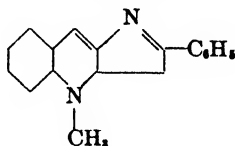
Black pigments have been produced by Giua<sup>303</sup> from pyrrole and oxalyl chloride, (COCl)<sub>2</sub>. Pyrrole (6.4 g.) dissolved in absolute ethyl ether (100 cc.) at -6°C. is treated with oxalyl chloride (12 g.). The temperature is allowed to rise and the mixture is heated on the water bath. Hydrochloric acid is evolved in the reaction and a black pigment precipitates out. This pigment is infusible and amorphous, soluble in hot concentrated inorganic acids. Another brown infusible, insoluble pigment is formed when the liquid from the above reaction is evaporated to dryness and the residue extracted with ether and benzene.

Sanna and Chessa<sup>304</sup> prepared pyrrole- $\alpha$ -ketomethylcarbinol ethyl ether, C<sub>8</sub>H<sub>11</sub>NO<sub>3</sub>, by the action of ethylglycolyl chloride on magnesylpyrrole in anhydrous ethyl ether. The compound is a thick, brown liquid which forms with hydriodic acid a black, insoluble resin. Resinification of 3-carbethoxy-2,4-dimethylpyrrole-5, $\beta$ -acrylic acid,



occurs when it is treated with hydrogen bromide and glacial acetic acid.<sup>305</sup>

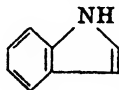
Robinson<sup>306</sup> reports that 2,3-(2'-phenylpyrrolo-4',5')-N-methyl-quinoline,



resinifies when heated above 100°C.

#### RESINS FROM INDOLE

Indole, C<sub>8</sub>H<sub>7</sub>N, or benzopyrrole, contains a benzene nucleus condensed with a pyrrole nucleus. It is a solid melting at 52°C.



and boiling with partial decomposition at 245°C. Like pyrrole it is easily resinified with hydrochloric acid.<sup>307</sup> The action of dry hydrogen chloride on a solution

<sup>301</sup> Q. Mingoa, *Gazz. chim. ital.*, 1932, 62, 844; *Chem. Abs.*, 1933, 27, 503.

<sup>302</sup> B. Oddo and Q. Mingoa, *Gazz. chim. ital.*, 1932, 62, 299; *Brit. Chem. Abs. A*, 1932, 753.

<sup>303</sup> M. Giua, *Gazz. chim. ital.*, 1924, 54, 593; *Chem. Abs.*, 1925, 19, 280.

<sup>304</sup> A. Sanna and G. Chessa, *Gazz. chim. ital.*, 1928, 58, 121; *Chem. Abs.*, 1928, 22, 2502.

<sup>305</sup> W. Küster, E. Brudi and S. Koppenhöfer, *Ber.*, 1925, 58, 1014; *J.C.S.*, 1925, 128 (1), 972. Cf.

H. Fischer and B. Walach, *ibid.*, 2818; *Chem. Abs.*, 1926, 20, 1620.

<sup>306</sup> G. M. Robinson, *J.C.S.*, 1929, 2951.

<sup>307</sup> G. Ciamician and C. Zatti, *Ber.*, 1889, 22, 1977.

of indole in benzene yields the colorless diindole hydrochloride<sup>200</sup> melting at 145-150°C. Free diindole has been obtained as an amorphous mass (m.p. 100-102°C.) by treating the hydrochloride with ammonium hydroxide.<sup>200</sup> Triindole has been formed by the action of metaphosphoric acid on indole,<sup>210</sup> and by the interaction of indole and diindole hydrochloride.<sup>211</sup> It has also been recovered from the residue of the distillation of indole.<sup>212</sup> Oddo<sup>213</sup> found that if a 10 per cent alcoholic solution of indole is exposed to air and sunlight for 2 months, a yellow compound,  $C_{16}H_{15}ON_3$ , is formed. If this compound is treated with hydrochloric acid it is converted into a resin.

Resinification occurs when 7-methylindole is treated with benzoylchloride and when 5- and 7-methylindoles are shaken with hydrochloric acid (5 per cent).<sup>214</sup> In benzene solution, 1- and 7-methylindoles polymerize when treated with hydrogen chloride, and although 3-methylindole (skatole) behaves similarly, 3-ethylindole does not.<sup>215</sup>

In the preparation of indole derivatives by the Grignard reaction, resinous substances often result. Indolylmagnesium iodide and ethyl acetate react to form 1-acetylindole which partly resinifies<sup>216</sup> when heated to 300-350°C. A small amount of pitch and a considerable amount of a red amorphous powder (insoluble in water and in ether) are formed when magnesylindole and phthalylchloride react in ether solution.<sup>217</sup> The ethyl ester of  $\beta$ -indoleglyoxylic acid (from magnesylindole and ethyl chloro-oxylate) reacts with benzene diazonium chloride to give an unstable compound which resinifies easily.<sup>218</sup> Magnesylmethylketole is oxidized by hydrogen peroxide to 3-hydroxy-2-methylindole (m.p. 40°C.) which quickly decomposes to a black, sticky mass.<sup>219</sup> Resinous bodies are formed in the preparation of  $\beta$ -indolylacetonitrile from indolylmagnesium iodide and chloroacetonitrile in cold anisole.<sup>220</sup>

Oxalyl chloride and 2-methylindole react to form crystalline 2-methyl-3-indoleglyoxyl chloride which when heated in neutral solvents yields a magenta-red resin.<sup>221</sup> Reduction of the oxime of 2-methylindole-3-aldehyde yields the corresponding amine. If hydrochloric acid is added to an ether solution of this amine, a resin precipitates out in 25 per cent yield.<sup>222</sup> An extensive study of the condensation of indole derivatives with aldehydes has been made by Burr,<sup>223</sup> in his investigations on humin formation. Resinous substances were obtained in many cases. Blount and Robinson<sup>224</sup> describe  $\beta$ -3-dihydroindolylpropionic acid as a pale, viscous oil, and its crude benzoyl derivative (formed by action of benzoyl chloride) as a gum.  $\gamma$ -3-Dihydroindolylbutyric acid and its benzoyl derivative are both resinous.

Isatin can be considered a derivative of indole because it is formed by the

<sup>200</sup> K. Keller, *Ber.*, 1913, 46, 726; *J.C.S.*, 1913, 104 (1), 403. See also B. Oddo, *Gazz. chim. ital.*, 1912, 43 (1), 385; *J.C.S.*, 1913, 104 (1), 755.

<sup>209</sup> O. Schmits-Dumont and B. Nicolajannis, *Ber.*, 1930, 63, 323; *Chem. Abs.*, 1930, 24, 2746.

<sup>210</sup> R. Weisgerber, *Ber.*, 1911, 44, 1140.

<sup>211</sup> O. Schmits-Dumont and others, *J. prakt. Chem.*, 1931, (2) 131, 146; 132, 39; *Brit. Chem. Abs. A*, 1931, 1165, 1429.

<sup>212</sup> K. Keller, *loc. cit.* For suggested structures of di- and triindole see B. Oddo and G. B. Crippa, *Atti. accad. Lincei*, (5) 33 (1), 31; *J.C.S.*, 1924, 126 (1), 427.

<sup>213</sup> B. Oddo, *Gazz. chim. ital.*, 1916, 46 (1), 323; *J.C.S.*, 1916, 110 (1), 502.

<sup>214</sup> O. Kruber, *Ber.*, 1926, 59, 2752; *Chem. Abs.*, 1927, 21, 912.

<sup>215</sup> O. Schmits-Dumont and K. H. Geller, *Ber.*, 1933, 66, 766; *Chem. Abs.*, 1933, 27, 3710.

<sup>216</sup> N. Putochin, *Ber.*, 1926, 59, 1987; *Chem. Abs.*, 1927, 21, 86. See also R. Majima and T. Shigematsu, *Ber.*, 1924, 57, 1449; *Chem. Abs.*, 1925, 19, 279.

<sup>217</sup> B. Oddo, *Gazz. chim. ital.*, 1923, 53, 569; *Chem. Abs.*, 1929, 23, 1634.

<sup>218</sup> B. Oddo and A. Albanese, *Gazz. chim. ital.*, 1927, 57, 827; *Chem. Abs.*, 1928, 22, 1776.

<sup>219</sup> F. Ingraffia, *Gazz. chim. ital.*, 1933, 63, 176; *Chem. Abs.*, 1933, 27, 3710.

<sup>220</sup> R. Majima and T. Hoshino, *Ber.*, 1925, 58, 2042; *J.C.S.*, 1925, 128 (1), 1450.

<sup>221</sup> M. Gius, *Gazz. chim. ital.*, 1924, 54, 593; *J.C.S.*, 1924, 126 (1), 1107.

<sup>222</sup> N. Putochin, *loc. cit.*

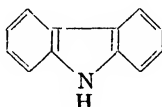
<sup>223</sup> G. O. Burr, with R. A. Gortner, *J.A.C.S.*, 1924, 46, 1224. Many references to earlier work with aldehydes and ketones are given here.

<sup>224</sup> B. K. Blount and R. Robinson, *J.C.S.*, 1931, 3158.

oxidation of indigo blue and also by the oxidation of oxindole. Resins have resulted from the condensation of isatin with various ketones<sup>226</sup> such as furfurylidene-acetone, methylcinnamylvinyl ketone and benzalethyl ketone. Resinification of isatin and of N-methyl isatin occurs when they are used as catalysts in the dehydrogenation of amino acids.<sup>226</sup> Silver isatin and benzoyl chloride react in benzene or in ether to form isatoid (m.p. 178-182°C) which can be obtained in crystalline form only from acetic acid solution. When dissolved in any other solvent it is precipitated as an oil by the addition of water. Evaporation of these solutions yields brilliant reddish-yellow lac-like residues.<sup>227</sup>

#### RESINS FROM CARBAZOLE

Carbazole, or dibenzopyrrole,



is a stable compound melting at 238°C. It occurs in crude anthracene obtained from coal tar. Perkin and Tucker<sup>228</sup> found that when potassium permanganate is added to a hot solution of carbazole in acetone a vigorous oxidation reaction sets in, giving a small yield of crystalline isomeric bicarbazoles and a major yield of an amorphous substance (m.p. 175°C). This substance was investigated by McLintock and Tucker,<sup>229</sup> who found that treatment with hydriodic acid for 20 hours at 150°C. gave as the principal reduction product a substance identical with carbazole. There was also formed in the reduction a small amount of a cream-colored amorphous mass (m.p. 300-310°C.).

Resinous products are produced by the reaction between carbazole (or its derivatives) and olefins containing 3 or more carbon atoms.<sup>230</sup> The reaction is carried out under pressure in an inert solvent, using a contact agent such as aluminum chloride or fuller's earth. Soft resins are formed from propylene and carbazole and from propylene and N-ethylcarbazole, whereas from carbazole and cyclohexene a hard resin results. These bodies are presumed to be mono- or polyalkylated carbazoles. Pale, transparent resins can be obtained from such products by condensation with aldehydes using sulphuric or hydrochloric acid as the condensing agent.<sup>231</sup> Diisopropylcarbazole when condensed with formaldehyde yields a resin melting at 95°C. Sulphonation of the alkylated carbazoles produces materials which can be used to increase the wetting and emulsifying power of aqueous solutions.<sup>232</sup>

#### RESINS FROM ALKALOIDS

An attempt has been made here to classify some of the many resinous materials obtained from alkaloid derivatives. Because of the variety of reactions involved

<sup>226</sup> H. John and F. Kahl, *J. prakt. Chem.*, 1928, 113, 14; *Chem. Abs.*, 1928, 22, 1160.

<sup>226</sup> W. Lagenbeck, *Ber.*, 1927, 60, 930; *Chem. Abs.*, 1927, 21, 2126.

<sup>227</sup> A. Hantzsch, *Ber.*, 1925, 58, 685; *Chem. Abs.*, 1925, 19, 2050.

<sup>228</sup> W. H. Perkin, Jr. and S. H. Tucker, *J.C.S.*, 1921, 119, 217.

<sup>229</sup> J. McLintock and S. H. Tucker, *J.C.S.*, 1927, 1219. See also G. E. K. Branch and W. W. Hall, *J.A.C.S.*, 1924, 46, 443.

<sup>230</sup> R. Michel, U. S. P. 1,916,629, July 4, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4700. U. S. P. 1,972,232, Sept. 4, 1934; *Chem. Abs.*, 1934, 28, 6444. British P. 327,746, 1928; *Brit. Chem. Abs. B*, 1930, 625. German P. 550,494, 1927; *Chem. Abs.*, 1932, 26, 4065. French P. 661,718, 1928; *Chem. Abs.*, 1930, 24, 1236.

<sup>231</sup> R. Michel, F. Frick and H. Buschmann, German P. 552,605, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5778. British P. 354,840, 1930; *Brit. Chem. Abs. B*, 1931, 1019.

<sup>232</sup> R. Michel and H. Buschmann, German P. 552,606, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5714.



only brief mention is made of the methods by which the resinous substances are obtained. The original work should be consulted for details. Resinous masses have been obtained from some of the derivatives of aporphine alkaloids<sup>233</sup> and from the methohalides of various derivatives of strychnidine,<sup>234</sup> brucidine<sup>235</sup> and neostrychnidine.<sup>236</sup> In efforts to synthesize alkaloids similar to protopine, resins were formed from the derivatives of homopiperonylic acid.<sup>237</sup> The derivatives of pseudoaconine and pseudoaconitine<sup>238</sup> and of sparteine<sup>239</sup> have yielded varnish-like materials in various reactions.

The following alkaloid derivatives have been described as resinous in character: neopine,<sup>240</sup> dibromoniquine,<sup>241</sup> tetrahydro-normethylmorphinethine,<sup>242</sup> and the hydrochloride of N-tryptamine (from calycanthine).<sup>243</sup> Certain alkaloid derivatives are sometimes obtained in crystalline or powdery form, but later resinify on air-exposure. Among these are quinotoxineoxime,<sup>244</sup> derivatives of quinineamine,<sup>245</sup> akuammine perchlorate,<sup>246</sup> and dihydrodesoxycinchonine.<sup>247</sup> Amorphous products have been obtained in the reduction of  $\alpha$ -chlorocodide (from codeine),<sup>248</sup> and in the oxidation of quebrachamine<sup>249</sup> and of hydroxyacanthine.<sup>250</sup>

If the hydrochloride of hydroxyacanthine is dissolved in dilute potassium hydroxide and then concentrated potassium hydroxide is added, the potassium salt separates as a resinous mass. The methyl ether of hydroxyacanthine is also resinous.<sup>251</sup> A gum is formed when protoberberinium chloride is heated in potassium hydroxide solution.<sup>252</sup> The hydrochloride of the methyl ester of lupinic acid (from lupinine) is converted into a resin by thionyl chloride.<sup>253</sup> Diversine produces resinous substances in its reaction with benzoic acid, phenylhydrazine, ethyl chloroformate and with bromine in glacial acetic acid.<sup>254</sup> Many of the alkaloid salts of the hydrogen phthalate of n-propylvinylcarbinol and of the hydrogen succinate of ethylvinylcarbinol are of a gummy nature.<sup>255</sup> Resinous or tarry products are formed when cocaine is heated with p-nitrobenzyl chloride or with saligenin.<sup>256</sup>

Amorphous substances have been formed in many cases in the condensation of aromatic aldehydes with  $\alpha$ -hydroxylepidine and with  $\gamma$ -hydroxyquinaldines.<sup>257</sup> Similarly, gummy materials have resulted from the condensation of formaldehyde with 1-benzyl-1,2,3,4-tetrahydro isoquinoline,<sup>258</sup> and of methylal with 1-homo-

<sup>233</sup> J. M. Gulland, R. D. Haworth and others, *J.C.S.*, 1928, 586; 1929, 658, 1666.

<sup>234</sup> G. R. Clemon, W. H. Perkin, Jr., and R. Robinson, *J.C.S.*, 1927, 1609, 1620.

<sup>235</sup> J. M. Gulland, W. H. Perkin, Jr., and R. Robinson, *J.C.S.*, 1927, 1647, 1655, 1656, 1657.

<sup>236</sup> O. Achmatowicz, W. H. Perkin, Jr., and R. Robinson, *J.C.S.*, 1932, 491, 496, 498.

<sup>237</sup> T. S. Stevens, *J.C.S.*, 1927, 182, 184, 187.

<sup>238</sup> T. M. Sharp, *J.C.S.*, 1928, 3094.

<sup>239</sup> K. Winterfeld, with F. W. Holschneider, *Arch. Pharm.*, 1929, 267, 433; *Chem. Abs.*, 1929, 23,

5187; *ibid.*, 1928, 266, 299; *Brit. Chem. Abs. A*, 1928, 806.

<sup>240</sup> C. F. van Duin, R. Robinson and J. C. Smith, *J.C.S.*, 1926, 906.

<sup>241</sup> J. Suzko, *Roczniki Chem.*, 1925, 5, 358; *Chem. Abs.*, 1926, 20, 1993.

<sup>242</sup> J. von Braun and R. S. Cahn, *Ann.*, 1926, 451, 55; *Chem. Abs.*, 1927, 21, 1124.

<sup>243</sup> R. H. F. Manske, *Can. J. Research*, 1931, 5, 592; *Chem. Abs.*, 1932, 26, 725.

<sup>244</sup> S. Frankel and N. Diamont, *Ber.*, 1925, 58, 554; *J.C.S.*, 1925, 128 (1), 574.

<sup>245</sup> S. Frankel, C. Trutt, M. Mehrer and O. Herschmann, *Ber.*, 1925, 58, 544; *Chem. Abs.*, 1925, 19,

2055.

<sup>246</sup> T. A. Henry and T. M. Sharp, *J.C.S.*, 1927, 1955.

<sup>247</sup> C. Schöpf, O. Thoma, E. Schmidt and W. Braun, *Ann.*, 1928, 465, 97; *Chem. Abs.*, 1928, 22,

4532.

<sup>248</sup> E. Mosettig, F. L. Cohen and L. F. Small, *J.A.C.S.*, 1932, 54, 793.

<sup>249</sup> E. Field, *J.C.S.*, 1924, 125, 1449.

<sup>250</sup> J. Gadamer and W. von Bruchhausen, *Arch. Pharm.*, 1920, 264, 193; *Brit. Chem. Abs. A*, 1926,

627.

<sup>251</sup> E. Späth and A. Kolbe, *Ber.*, 1925, 58, 2284; *Chem. Abs.*, 1926, 20, 1085.

<sup>252</sup> S. N. Chakravarti, R. D. Haworth and W. H. Perkin, Jr., *J.C.S.*, 1927, 2275.

<sup>253</sup> C. Schöpf, O. Thomä, E. Schmidt and W. Braun, *loc. cit.*

<sup>254</sup> H. Kondo and T. Nakazato, *J. Pharm. Soc. Japan*, 1924, 511, 691; *Chem. Abs.*, 1925, 19, 1708.

<sup>255</sup> J. Kenyon and D. R. Snellgrove, *J.C.S.*, 1925, 127, 1169.

<sup>256</sup> W. H. Gray, *J.C.S.*, 1925, 127, 1154, 1155.

<sup>257</sup> J. Tröger and E. Dunker, *J. prakt. Chem.*, 1925, 109, 88; *Chem. Abs.*, 1925, 19, 1278.

<sup>258</sup> S. N. Chakravarti, R. D. Haworth and W. H. Perkin, Jr., *loc. cit.*

piperonyl-6,7-dimethoxytetrahydro isoquinoline.<sup>299</sup> A gummy compound is derived by the action of formaldehyde on 6'-nitroveratrylnorhydrohydrastinine.<sup>300</sup> In studies on the constitution of isochondodendrine it has been found that the trimethyl ester of 3,4-dimethoxy,1,1'-diphenylether-5,6,3'-tricarboxylic acid is a resinous substance.<sup>301</sup>

<sup>299</sup> J. S. Buck and W. H. Perkin, Jr., *J.C.S.*, 1924, 125, 1682.

<sup>300</sup> R. D. Haworth and W. H. Perkin, Jr., *J.C.S.*, 1925, 127, 1448.

<sup>301</sup> F. Faltis and K. Zwerina, *Ber.*, 1929, 62, 1039; *Chem. Abs.*, 1929, 23, 4222.

## Chapter 36

### Resins from Wood and from Carbohydrates

The resins considered in this chapter are representative of some of the progress made in the utilization of waste products from wood and other plant materials. Because of undesirable properties possessed by many of them they have been used but little. The resins from carbohydrates, included at the end of the chapter, are probably of more interest than the others.

Wood consists principally of cellulose, lignin and sap, the latter containing resins and dissolved material. An extensive study of the composition of lignin has been made by Klason<sup>1</sup> who has found two principal constituents:  $\alpha$ -lignin,  $(C_{10}H_{10}O_4)_n$ , 64 per cent, and  $\beta$ -lignin,  $C_{10}H_{12}O_4(C_6H_7O_2COCH_3)_n$ , 36 per cent. The average lignin content of wood is about 26 per cent. Willstätter and Kalb<sup>2</sup> observed in their studies on lignin that boiling hydriodic acid and phosphorus convert it into a colorless, weakly acid resin, soluble in alcohol and acetic acid.

In the investigations of Legeler<sup>3</sup> it was noted that treatment of wood with phenol and small amounts of hydrochloric acid freed the wood from lignin but at the same time caused the formation of resins from the condensation of phenol and lignin. This reaction was also noticed by Jonas<sup>4</sup> who described the phenol-lignin as an amorphous, brown product.

Various resins have been produced by the action of phenols on lignin-containing materials, particularly wood. For instance, phenols and sawdust, using as catalyst either sulphuric or hydrochloric acid, yield a product resembling asphalt or pitch.<sup>5</sup> In the process of Hartmuth,<sup>6</sup> resinous materials for lacquers or adhesives are produced. Wood is heated with phenols either in concentrated form or diluted with water, alcohol or liquid hydrocarbons, the phenol combining with the lignin of the wood and leaving the cellulose unchanged. Catalysts include inorganic or organic acids and acid substances such as the chlorides of tin, zinc or aluminum and also ammonium chloride. The phenol-lignin compound contains free hydroxyl groups and can be methylated.<sup>7</sup>

The phenolic digestion of wood under pressure yields a resinous derivative of phenol and cellulose.<sup>8</sup> Wood flour is heated with 4 times its weight of phenol at 250°C. for from 2 to 20 hours depending on the product desired. Uncom-

<sup>1</sup> P. Klason, *Ber.*, 1929, 62, 2523; 1930, 63, 792; 1931, 64, 2733; *Brit. Chem. Abs. A.*, 1929, 1248; *Chem. Abs.*, 1930, 24, 3496; 1932, 26, 1355.

<sup>2</sup> R. Willstätter and L. Kalb, *Ber.*, 1923, 55, 2637; *Chem. Abs.*, 1923, 17, 982.

<sup>3</sup> E. Legeler, *Cellulosechem.*, 1923, 4, 61; *Chem. Abs.*, 1923, 17, 3249.

<sup>4</sup> K. G. Jonas, *Z. angew. Chem.*, 1921, 34, 289; *Chem. Abs.*, 1921, 15, 3663. See also W. Schrauth, and K. Quasebarth, *Ber.*, 1924, 57, 854; *Chem. Abs.*, 1924, 18, 3053.

<sup>5</sup> G. Hübner and E. Kárpáti, *French P.* 643,766, 1927; *Chem. Abs.*, 1929, 23, 1748. *British P.* 293,963, 1927; *Chem. Abs.*, 1929, 23, 3060.

<sup>6</sup> R. Hartmuth, *German P.* 328,705, 1919, and its addition 328,783, 1919; *J.S.C.I.*, 1921, 40, 144A, 212A.

<sup>7</sup> Y. I. Chulkov, I. A. Speranskaya and V. K. Kusnetsov, *Plast. Massui*, 1934 (2), 16; *Chem. Abs.*, 1934, 28, 6326.

<sup>8</sup> E. E. Notovny and C. J. Romieux, *U. S. P.* 1,731,315, July 16, 1929, to J. S. Stokes; *Chem. Abs.*, 1929, 23, 4357. See *Plastics*, 1930, 6, 149.

bined phenol is removed by distillation leaving behind a brownish-black resin of high melting point. If the period of heating is short, some of the wood remains undigested and can serve as a filler for molding. Modification of the product was effected by the addition of ammonia or various aldehydes. A small amount of sulphuric acid may be employed to accelerate reaction.<sup>9</sup>

A somewhat similar method was used by Prentiss<sup>10</sup> Wood, in finely divided form (100 parts), is digested with phenol (29 parts) in alkaline solution (12 parts ammonium hydroxide, sp. gr. 0.90, in 800 parts of water) for 4 hours under a pressure of 200-300 pounds per square inch. The reaction product is boiled for 1 hour under reflux after a solution of formaldehyde (29 parts in 43 parts of water) has been added. The solid material is then freed from liquids and molded into desired shapes using a pressure of 1000 pounds per square inch at 150°C. A composition for high-pressure molding is formed by the action of phenol (10 parts) on finely ground wood (100 parts) using hydrochloric acid (0.3 part) as a catalyst.<sup>11</sup>

Peanut hulls were utilized for resin production by Jones<sup>12</sup> who heated them with phenols and acid. A black sticky mass was formed, which was ground under water, boiled and washed to remove acidic substances. Barium carbonate<sup>13</sup> is also recommended to neutralize the mixture. The ground material, after drying, can be hot-molded. Wood shavings, oat and cottonseed hulls, corn cobs and cotton are other cellulosic materials that may be substituted. Use of an aldehyde hardening agent is reported to yield a highly resistant plastic substance.

Wood pulp from hemlock or spruce was disintegrated and treated with phenol or cresol by Lowen and Benson.<sup>14</sup> Hydrochloric acid was added and the whole mass heated 6 hours at 70°C., air-dried for several days and ground in a ball mill. The powder was then heated at about 80°C. to plasticize it, molded and finally baked at a rising temperature (up to 150°C.) till hard. Some results obtained by these investigators are given in Table 35.

TABLE 35.—Composition of Wood Pulp Plastics.

Pulp	Phenol	Cresol	Acid	Plasticizer	Remarks
g.	g.	g.	g.		
175	175	..	18	None	Hard, black solid
50	66	..	10	None	Similar to above
50	..	38	10	None	Hard but slightly brittle
50	..	25	10	None	Brittle
50	..	62.5	10	None	Hard, slightly brittle
50	..	75	10	None	Very plastic. Hard after baking
50	..	62.5	10	Castor oil	Strong and hard
50	..	62.5	10	Glycerol	Very strong

Lignin also has been condensed with aldehydes and amines to give resinous products. Black resins of various degrees of hardness and luster were obtained from lignin (from corn cobs) and aromatic amines, including aniline, o- and p-toluidine, benzidine and  $\alpha$ - and  $\beta$ -naphthylamine.<sup>15</sup> As a part of the same experimental work black resins were made from lignin and furfural, using as a catalyst either hydrochloric acid, calcium oxide, sodium carbonate or pyridine. Similarly, a molding composition is formed by heating furfural and hydrolyzed

<sup>9</sup> E. E. Novotny and C. J. Kendall, U. S. P. 1,886,353, Nov. 1, 1932, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 1531. See also Canadian P. 249,166, 1925; *Chem. Abs.*, 1925, 19, 3166 and British P. 203,193, 1922; *J.S.C.I.*, 1924, 43, 141B.

<sup>10</sup> S. W. Prentiss, U. S. P. 1,892,409, Dec. 27, 1932, to Potlatch Forests, Inc.; *Chem. Abs.*, 1933, 27, 2300.

<sup>11</sup> E. C. Sherrard and E. Beglinger, U. S. P. 1,923,756, Aug. 22, 1933, to the U. S. Gov't. and People; *Chem. Abs.*, 1933, 27, 5493.

<sup>12</sup> L. R. Jones, U. S. P. 1,917,038, July 4, 1933; *Chem. Abs.*, 1933, 27, 4640.

<sup>13</sup> L. R. Jones, U. S. P. 1,961,588, June 5, 1934; *Chem. Abs.*, 1934, 28, 4849.

<sup>14</sup> L. Lowen and H. K. Benson, *Ind. Eng. Chem.*, 1934, 26, 1273.

<sup>15</sup> M. Phillips and H. D. Weihe, *Ind. Eng. Chem.*, 1931, 23, 286. M. Phillips, U. S. P. 1,750,903, March 18, 1930; *Chem. Abs.*, 1930, 24, 2623. A varnish of furfural and lignin in various solvents has also been made by I. Phillips (U. S. P. 1,890,526, Feb. 28, 1933; *Chem. Abs.*, 1933, 27, 3098).

wood with a mineral acid as catalyst.<sup>16</sup> Wood is hydrolyzed with steam (pressure 120 pounds per square inch) in the presence of 3 per cent sulphuric acid. The resulting fibrous material (100 parts) is acidified with hydrochloric acid (0.5 part), mixed with furfural (5 parts) and molded at 120°C. under a pressure of 2000 pounds per square inch. Within 15 minutes a hard resinous product is secured. If one part of an aromatic amine is added to the mixture before molding the water-resistant qualities are improved.

Fiberboard may be manufactured by treating cellulosic material in aqueous suspension with an agent (urea, phenols or aldehydes) capable of combining with the cellulose. By sheeting the fibrous mass, drying and subjecting to heat and pressure, hard boards are secured.<sup>17</sup>

In the method of Lauter<sup>18</sup> finely divided wood (sawdust) is acted on by an aldehyde, but reaction does not take place with the lignin of the wood but rather with the natural resins it contains. For this reason pine or spruce wood is used. The finely divided wood is moistened with formaldehyde or acetaldehyde and then molded at 115°C. under 1000 pounds pressure. Ushakov and Freidberg<sup>19</sup> prepared plastic materials from birch or fir sawdust by treatment with phenol before condensing with formaldehyde. Stein<sup>20</sup> condensed the nitro and acetyl derivatives of cellulose with phenols and aldehydes to prepare resins.

It may be of interest to note here certain methods of recovering the natural resin from resin-rich wood. If wood such as Swedish pine is heated under pressure with concentrated alkali and sodium chloride solution, it disintegrates, and the resins are converted into alkali salts.<sup>21</sup> Fatty acids and lignin are precipitated with the resin, but their properties are sufficiently related to those of the resin to have no harmful effect in its use. According to König,<sup>22</sup> if wood is heated under pressure with dilute mineral acids or dilute alkalies, a liquid is obtained from which resins can be precipitated by the addition of ammonium hydroxide or calcium carbonate.

The action of mineral esters of polyhydric alcohols on such substances as wood, straw or peat furnishes compositions said to be useful as coating or binding materials.<sup>23</sup> For instance, the residue from the saccharification of peat when heated with ethylene dichloride at 140°C. in an autoclave gave a solution which may be applied directly to wood or mixed with varnishes. Evaporation of the solution yielded asphaltic materials, but if water or a salt or alkaline solution is added a finely powdered pigment is formed. Residues from the saccharification of peat or wood may be converted also into plastic materials by mixing with sulphur, tars or pitch.<sup>24</sup> The coatings or molded articles produced in this way are reported to be resistant to acids.

A resin suggested as a substitute for natural resins (pitch, asphalt and lac) is made from wood, wood waste or grass<sup>25</sup> by heating with phenol to a sufficient

<sup>16</sup> E. C. Sherrard and E. Beglinger, U. S. P. 1,932,255, Oct. 24, 1933, to the U. S. Gov't. and People; *Chem. Abs.*, 1934, 28, 592.

<sup>17</sup> British P. 407,161, Mar. 15, 1934, to Aktiebolaget Mo och Domsjö Wallboard Co.; *Chem. Abs.*, 1934, 28, 5205.

<sup>18</sup> F. Lauter, U. S. P. 1,697,248, Jan. 1, 1929, and 1,702,013, Feb. 12, 1929, to Lignel Corp.; *Chem. Abs.*, 1929, 23, 1242, 1483. French P. 663,640, 1928; *Chem. Abs.*, 1930, 24, 707.

<sup>19</sup> S. Ushakov and E. Freidberg, *Kunststoffe*, 1934, 24, 277; *Chem. Abs.*, 1935, 29, 2257.

<sup>20</sup> C. Stein, French P. 673,289, 1929; *Chem. Abs.*, 1930, 24, 3662.

<sup>21</sup> German P. 315,731, 1916, to Aktiebolaget Cellulosa; *J.S.C.I.*, 1920, 39, 307A.

<sup>22</sup> J. König, British P. 8006, 1914; *Chem. Abs.*, 1916, 10, 75.

<sup>23</sup> R. Griessbach and E. Koch, German P. 525,089, 1923, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4138.

<sup>24</sup> French P. 685,567, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5950.

<sup>25</sup> C. Glaessen, British P. 160,482, 1919; *Chem. Abs.*, 1921, 15, 2355.

degree only to open up the fibers. The cellulose is separated and excess phenol removed from the residue.

Treatment of finely-divided wood with an alkylene oxide (at temperatures up to 180°C.) in the presence of a weak base or acid gave materials which may be molded into desired shapes.<sup>30</sup> Wood in pieces may be treated similarly, yielding a non-porous product said to be superior to the initial wood in mechanical properties. Insoluble plastic bodies are formed when cork meal is suspended in an inert medium such as chlorobenzene and esterified with acetic anhydride or phosphorus oxychloride in pyridine.<sup>31</sup>

The treatment of cellulose or other vegetable matter with a specific enzyme from latex yields a substance which may be polymerized or hardened by the action of an aldehyde or ketone in either alkaline or acid mediums. The resultant product<sup>32</sup> is reported to resemble rubber in its properties. A modification in the procedure involves maceration of the plant matter in sodium bisulphite and phenol solutions.<sup>33</sup>

Substances resembling horn in texture have been obtained by Schorger in studies on the gelatinization of lignocellulose.<sup>30</sup> Both hard and soft woods were gelatinized with dilute alkali and then flocculated with acetic acid. The mass was washed and dried at 30-40°C., yielding the horn-like material. A neutralized suspension of gelatinized aspen when spread on a smooth surface and allowed to dry at room temperature yielded a pale yellow, translucent film. A product resembling horn has also been formed from lichenin (from Iceland moss).<sup>34</sup> The pentanitrate was produced by the action of nitric and sulphuric acids and then gelatinized with a solvent.

According to Berl and Biebesheimer,<sup>35</sup> cotton treated with alkalis (e.g., N-caustic soda solution) at 310-330°C. under 180-200 atmospheres pressure is converted into carbon dioxide, hydrogen and a highly viscous material which on exposure to air became a black resinous mass, slightly soluble in alcohol and ether and very soluble in acetone. Hydrogenation of this mass at 420-460°C. yielded a liquid resembling petroleum.

Concentrated sulphurous acid reacts with lignocellulose to furnish soluble lignone derivatives. Oxidation of a solution of these derivatives with chromium oxide gives rise to insoluble gel-like materials.<sup>36</sup> If the gels are used to impregnate wood or fabrics they may be formed within the structure of the wood or fabric by controlling the temperature of the solution. To illustrate, a mixture of the lignone solution and chromic acid is made and immediately applied to wood. If the temperature is kept at about 16°C. gel formation will not occur for 24 hours. Viscous colloidal solutions have also been obtained by the action of triphenylchloromethane on cellulose or starch.<sup>34</sup>

Tanning compounds were obtained by Jaeger and Witzel<sup>37</sup> by the condensation of cellulose, phthalic anhydride or aldehydes, and aromatic hydrocarbon residues, using sulphuric acid as a catalyst. A lighter color may be secured by bleaching the product with chlorine or sodium hypochlorite.

<sup>30</sup> H. Suida, *Austrian P.* 125,229, 1931; *Chem. Abs.*, 1932, 26, 1436.

<sup>31</sup> British P. 291,773, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 1268.

<sup>32</sup> F. Bailly, *French P.* 768 051, 1934; *Chem. Abs.*, 1935, 29, 643.

<sup>33</sup> F. Bailly, *French P.* 43,753, 1934, addn. to 768,051; *Chem. Abs.*, 1935, 29, 1684.

<sup>34</sup> A. W. Schorger, *Ind. Eng. Chem.*, 1923, 15, 812. See F. Fischer and H. Tropach (*Ges. Abhandl. Kennt. Kohle*, 1921, 6, 271; *J.S.C.I.*, 1924, 43, 169B) for the action of alkali on lignin.

<sup>35</sup> J. Reilly, M. Hayes and P. J. Drumm, *Proc. Roy. Irish Acad.*, 1931, 40B, 102; *Chem. Abs.*, 1932, 26, 433.

<sup>36</sup> E. Berl and H. Biebesheimer, *Am.*, 1933, 504, 33; *Brit. Chem. Abs. A.*, 1933, 929.

<sup>37</sup> C. F. Cross, *U. S. P.* 1,553,230, Sept. 8, 1925; *Chem. Abs.*, 1925, 19, 3594. *Canadian P.* 245,853, 1925; *Chem. Abs.*, 1925, 19, 1348.

<sup>38</sup> B. Helfferich and H. Koester, *Ber.*, 1924, 57, 587; *Chem. Abs.*, 1924, 18, 2373.

<sup>39</sup> A. O. Jaeger and E. W. Witzel, *U. S. P.* 1,941,475, Jan. 2, 1934, to Selden Co.; *Chem. Abs.*, 1934, 28, 1688.

## RESINS FROM WOOD DISTILLATION

Although the main constituents of pyroligneous acid are wood alcohol, acetic acid and tar there are also small amounts of aldehydes, ketones, amines and phenols. Methods of preparing phenol-aldehyde resins from pyroligneous acid were developed by Bardy and Duchemin.<sup>36</sup> One procedure consists in boiling tar-free pyroligneous acid under reflux for several hours, and another in heating phenolic oils with formaldehyde in hydrochloric acid.

The principal method is to pass pyroligneous acid vapors (freed from tar) into an absorption vessel containing alkali carbonates or milk of lime. In order to get the largest yield of resins, each absorption vessel is connected to a battery of retorts instead of to a single retort, because in such destructive distillation the bulk of aldehydic material is liberated before phenols. With a battery of retorts the phenolic vapors from the end of one distillation will meet the aldehyde vapors from the beginning of another. In each absorption vessel dark-colored liquids are formed which, when acidified, become yellow and then deposit a black resin (melting at 60-70°C.). The resin is soluble in alkalies and is reprecipitated by acids. It is also soluble in acetone, methyl alcohol and methyl acetate but the solubility is decreased by heating the resin to high temperatures. If it is heated to 200°C. and then cooled a hard, black mass of conchoidal fracture is obtained. Although the total yield of resin is only about 0.5% of the weight of wood used, the recovery of resin facilitates the purification of methyl alcohol and sodium acetate, which are the desired products from pyroligneous acid. Crude methyl alcohol gives a small amount of light-yellow resin when it is distilled over alkali. Resinous material is derived also from the mother-liquors of sodium acetate.

Resin formation in crude methyl alcohol by the action of alkalies was noticed also by Chute.<sup>37</sup> In his process of making wood alcohol the addition of excess alkali to a pyroligneous acid distillate resulted in the development of a yellow resin which (Chute suggested) could be used as a dyestuff since it imparted a bright-yellow color to organic material when properly applied.

Two kinds of tar are formed during the distillation of wood. As one is soluble in pyroligneous acid and the other is relatively insoluble they are distinguished by the terms "dissolved tar" and "settled tar." Hawley and Calderwood<sup>38</sup> have found through studies on tar from hard maple that dissolved tar contains a large proportion of phenolic and acidic constituents<sup>39</sup> and is sensitive to the decomposing or polymerizing action of heat at temperatures far below those at which portions of settled tar distil without decomposition.<sup>40</sup>

A molding resin has been made from the soluble tar of wood distillation by condensation with formaldehyde, trioxymethylene or hexamethylenetetramine.<sup>41</sup> A fraction of the tar taken between 195-250°C. is mixed with formaldehyde and heated under reflux for half an hour at 90-100°C. Then a small amount of ammonium hydroxide is added and heating is continued for 12 hours. In a typical example, 145 parts by weight of the tar fraction are used with 121 parts of formaldehyde (40 per cent solution) and ammonium hydroxide equivalent to 3 parts of ammonia. After 12 hours of heating a viscous oily layer is formed which is decanted from the aqueous mixture and heated for 2 hours in an open container at 170-180°C. The result is a

<sup>36</sup> P. Bardy, French P. 402,907, 1908, to Pages Camus et Cie.; *J.S.C.I.*, 1909, 28, 1330. German P. 234,806, 1908; *Chem. Abs.*, 1911, 5, 3175. R. P. Duchemin, *Bull. soc. chim.*, 1910, (4) 7, 473; *Chem. Abs.*, 1910, 4, 2873; *Bull. assoc. chim. suc. dist.*, 1910, 27, 1101; *J.S.C.I.*, 1910, 29, 748.

<sup>37</sup> H. O. Chute, U. S. P. 824,906, July 3, 1906; *Chem. Abs.*, 1907, 1, 114.

<sup>38</sup> L. F. Hawley and H. N. Calderwood, Jr., *Ind. Eng. Chem.*, 1925, 17, 149.

<sup>39</sup> In the opinion of R. P. Duchemin (*loc. cit.*) the tars of wood distillation are merely solutions of resins in unreacted phenols.

<sup>40</sup> See also G. Du Pont and J. L. Lussaud, *Bull. inst. pin.*, 1929, 301; *Brit. Chem. Abs. B*, 1931, 467; I. J. Postovski, N. A. Apollonov and B. P. Lukovkin, *Ann. inst. polytech. Oural*, 1927, 6, 241; *Chem. Abs.*, 1928, 22, 4787.

<sup>41</sup> J. C. Carlin and C. A. Hochwalt, U. S. P. 1,911,489, May 30, 1933, to Tennessee Products Corp.; *Chem. Abs.*, 1933, 27, 4111. Canadian P. 331,165, 1933; *Chem. Abs.*, 1933, 27, 3629.

dark brown resin, hard and not melting but capable of softening when heated. It may be mixed with fillers and molded into articles said to possess strength and good electrical- and heat-insulating properties. The resin is unaffected by acids and alkalies and is partially soluble in benzene or solvent naphtha.

In another procedure, the tar from coniferous wood is saponified with concentrated alkali, separated from unsaponified material and then warmed with formaldehyde.<sup>46</sup> The viscous mass obtained is washed with water and well dried. The resulting resin is soluble in solvent naphtha, forming a paint said to give moisture-resistant coatings.

A resinous material for varnishes has been produced by the hardening action of lime on pine-tar fractions, freed from oily constituents.<sup>48</sup> For instance, light pine tar is distilled at 100-160°C. with superheated steam until oily constituents are no longer obtained in the distillate. About 20 per cent of the tar is thus converted into a light distillate containing turpentine oil and 70 per cent remains as a viscous residue. The addition of 5 per cent calcium hydroxide hardens this residue and it can then be dissolved in a solvent to give varnishes, light to dark brown in color. It is reported that these varnishes dry rapidly to a glossy, but not sticky, finish.

A modification of the above procedure consists in substituting acids for alkalies.<sup>44</sup> Wood tar or wood-tar oil is treated with concentrated sulphuric acid and the resulting water-soluble substances are removed. After separation of oily constituents by steam, air or solvents, the residue is soluble in alcohol or acetone and can be used for black varnishes or paints. Coatings of this material are stated to be waterproof and resistant to alkalies, benzene or lubricating oils.

If wood tar is heated and agitated with chlorine (either liquid, aqueous or nascent) a brittle black-brown resinous mass results.<sup>45</sup> A rapidly drying varnish giving a lustrous coating is obtained by dissolving the resin in alcohol.

Hamburger<sup>46</sup> prepared a resin by heating wood tar with zinc oxide (or oxides of other heavy metals) at 110°C. As much as 12 per cent of zinc oxide can be added without injuring the properties of this resin. A binder for artificial stone was made by Flexer<sup>47</sup> by oxidizing wood tar, treating the product with concentrated alkali and then digesting it with a thinning medium (dilute ammonium hydroxide or alcohol). The solid product is washed with water and pressed dry. It is then melted and mixed with 4 to 5 times its weight of sand or gravel and molded into desired shapes.

A balsam-like viscous liquid has been obtained by Pallas<sup>48</sup> from pyroligneous acid tar. The tar is washed several times with boiling water and then made alkaline with calcium hydroxide and saturated with sulphur dioxide. A clear liquid results, which on evaporation yields a viscous balsam substance intended for use as a salve base and in textile finishing.

#### RESINS FROM WOOD-PULP MANUFACTURE

Many attempts have been made to recover resinous material from waste liquors in both the soda and sulphite processes of making wood pulp. Schmid<sup>49</sup> stated

<sup>42</sup> German P. 338,854, 1919, to Chem. Fabr. Flörsheim H. Noerdlinger; *J.S.C.I.*, 1921, 40, 742A. See also K. A. Lingner, French P. 329,971, 1903; *J.S.C.I.*, 1903, 22, 104.

<sup>43</sup> German P. 320,656, 1916, to Chem. Fabr. Flörsheim H. Noerdlinger; *Chem. Abs.*, 1921, 15, 1083.

<sup>44</sup> German P. 286,650 and 290,818, 1914, to Chem. Fabr. Flörsheim H. Noerdlinger; *J.S.C.I.*, 1916, 35, 106, 610.

<sup>45</sup> German P. 320,620, 1918, to J. D. Riedel A.-G.; *Chem. Abs.*, 1921, 15, 1990.

<sup>46</sup> S. Hamburger, German P. 324,876, 1917; *J.S.C.I.*, 1920, 39, 792A.

<sup>47</sup> A. S. Flexer, *Raw Materials Review*, 1922, 1, 180; *Chem. Abs.*, 1923, 17, 195.

<sup>48</sup> E. Pallas, *Pharm. Zentr.*, 1930, 71, 609; *Brit.-Chem. Abs. B*, 1930, 1054. *Chem. Tech. Rundschau*, 1930, 45, 578; *Chem. Abs.*, 1930, 24, 4382.

<sup>49</sup> W. Schmid, *Papier-Fabr.*, 1931, 29 (*Tech.-Wiss. Teil*), 1; *Chem. Abs.*, 1931, 25, 3165.



that the average yield of liquid rosin from alkali pulp waste liquors is 30 kg. per ton of pulp made, varying of course with the process and the type of wood used.

One method of extracting resins from liquors of the soda process was devised by Greenwood.<sup>50</sup> The alkaline liquor remaining after the digestion of wood is known as "black liquor," and contains all the non-cellulose constituents of the wood. Floating on the surface of the liquid is a foam known as "crude rosin soap," containing both saponified and unsaponifiable resins. The "soap" is brought into intimate contact with a solvent (petroleum ether, gasoline or naphtha) by emulsification. Upon the addition of a mineral acid, resin acids are released and dissolve in the solvent. The mixture is heated moderately, causing the solution of resin acids to float on top. This layer is treated with a second solvent (methyl alcohol) immiscible with the first. Abietic acid is selectively dissolved by the second solvent and the two layers are separated. Evaporation of the second solvent yields crystalline abietic acid which is converted into rosin by heating. The residue from recovery of the first solvent contains a less pure rosin.

A somewhat similar procedure was used by Bergström.<sup>51</sup> Resinates from the alkaline liquor are treated with sulphuric acid and then with turpentine oil (cold at first and then heated). A clear solution is formed which is distilled under vacuum to obtain resins. The black liquor from the alkaline digestion of esparto grass yields a coagulated resinous precipitate when treated with an excess of sulphuric acid.<sup>52</sup> The resin is insoluble in ether, oils and turpentine, but is soluble in acetic acid, acetone, phenol, alcohol, aniline and alkalies. Its use as a varnish and for sizing and waterproofing purposes has been suggested. Resin from black liquor can be mixed with fibrous material and small amounts of phenol resin and glue added to form a molding composition.<sup>53</sup>

French<sup>54</sup> recovered impure resin from alkaline liquors (used to digest resinous wood) by passing an acid gas, e.g., sulphur dioxide, into the liquor. A hydrocarbon solvent (benzene, toluene or gasoline) is used for purification by vacuum distillation. The precipitated resin may be converted into water-soluble resinates by treatment with sodium carbonate solution, followed by crystallization.<sup>55</sup>

Lange<sup>56</sup> obtained a binding agent for briquettes from the liquors produced by the action of sodium carbonate on finely-divided wood. A sludge containing resin-soap and lignin is deposited in the liquor when cooled. The soap is converted into large flocks by sodium hydroxide and then treated with sodium peroxide to oxidize the lignin. A binding agent is secured after the liquor has been treated for the recovery of soda.

A great deal of investigation has been made on the constituents of waste liquor from the sulphite process of pulp manufacture. Klason<sup>57</sup> has studied particularly the ligninsulphonic acids. Naphthylamine hydrochloride precipitates from the sulphite liquor substances known as  $\alpha$ -ligninsulphonic acids which melt at high temperatures to form a pitch. In cold water this pitch hardens to a friable resin. If a solution of a salt of  $\alpha$ -ligninsulphonic acid is treated with the hydrochlorides of hydroxylamine and  $\beta$ -naphthylamine a white precipitate is formed which when heated slightly yields a yellow resin.<sup>58</sup> A dark brown resin was found by König<sup>59</sup>

<sup>50</sup> F. E. Greenwood, U. S. P. 1,560,420, Nov. 3, 1925, to Pine Waste Products Inc.; *Chem. Abs.*, 1926, 20, 290. See U. S. P. 1,593,656, July 27, 1926; *Chem. Abs.*, 1926, 20, 3236.

<sup>51</sup> K. G. Bergström, French P. 633,416, 1928; *Chem. Abs.*, 1930, 24, 739.

<sup>52</sup> C. Biddle, *J.S.C.I.*, 1916, 35, 401.

<sup>53</sup> T. M. Vinson, German P. 538,799, 1929; *Chem. Abs.*, 1932, 26, 2318.

<sup>54</sup> E. H. French, U. S. P. 1,693,586, Nov. 27, 1928; *Chem. Abs.*, 1929, 23, 722.

<sup>55</sup> E. H. French, U. S. P. 1,889,405, Nov. 29, 1932; *Chem. Abs.*, 1933, 27, 1530.

<sup>56</sup> A. Lange, German P. 314,445, 1918; *J.S.C.I.*, 1920, 39, 241A.

<sup>57</sup> P. Klason, *Svensk. Kem. Tids.*, 1928, 40, 3; *Chem. Abs.*, 1928, 22, 3635.

<sup>58</sup> P. Klason, *Svensk. Kem. Tids.*, 1922, 25, 364; *Chem. Abs.*, 1923, 17, 3168. See also E. Häggland, *Cellulosechem.*, 1925, 6, 29; *J.S.C.I.*, 1925, 44, 441; *Papier-Fabr.*, 1926, 24, 449, 483; *Brit. Chem. Abs. B.*, 1928, 911.

<sup>59</sup> F. König, *Papier-Fabr.*, 1925, 23, 501; *J.S.C.I.*, 1925, 44, 753B

as a residue in the distillation of the oily layer from sulphite waste-liquor. Pinabietic acid,  $C_{10}H_{16}O_4$ , which resinifies readily, has been isolated from sulphite liquor by Aschan and Ekholm.<sup>60</sup> (Cf. abietic acid, Chapter 37.)

A plastic resin was produced by Wallace<sup>61</sup> by condensing sulphite waste-liquor with a phenol and aldehyde using ammonium chloride as a catalyst. The quantity of phenols used is at least 25 per cent, and that of aldehydes at least 5 per cent, of the amount of sulphite liquor. The resin is soluble in alcohol and insoluble in water.

Knight<sup>62</sup> suggests fermenting the liquor and removing the alcohol by distillation. The residue, on treatment with phenol or cresol, using various catalysts (hydrochloric acid, caustic soda or potash, lime, zinc chloride), yields a resinous condensation product which on further heating becomes insoluble. It is recommended for varnishes or as a shellac substitute. An interesting variation in this method is to retain the alcohol generated by fermentation and oxidize it to acetaldehyde by addition of potassium dichromate. The phenol is then added and a double condensation is carried out. In one example, fermented waste-liquor containing 100 g. of solids and 1 g. of alcohol was treated with 101 g. of phenol and 8 g. of potassium dichromate. The dichromate not only oxidized the alcohol, but the chromium salt derived in the reaction served as the condensing agent.

A method used by Schmidt<sup>63</sup> to make a resin from sulphite liquor consists in evaporating it to 25 per cent of its volume and treating the concentrate with chlorine for 2 hours. The precipitate is separated and oxidized with a chlorate and hydrochloric acid until the reaction product contains 20 per cent chlorine. The resulting material is stable and can be used as a tanning agent or as a substitute for natural resins. The process was modified by Stinnes<sup>64</sup> who used nitric acid or hydrogen peroxide as an oxidizing agent instead of the chlorate and hydrochloric acid.

Treatment of sulphite waste-liquor with a solution of water glass yields a gelatinous precipitate.<sup>65</sup> When this is dried a resinous substance is obtained which may be mixed with fillers for various purposes. For instance, by mixing it with blast-furnace slag a road-making or building material can be formed.

Several other methods have been suggested for the recovery of resins from sulphite liquor.<sup>66</sup> If the latter is treated with hydrogen sulphide and then with air and a small amount of nitric acid the resins collect in a scum on the surface. Separation of resins is also effected by the addition of crude salt to the liquor. A road-building material can be made by neutralizing sulphite liquor with sodium carbonate or calcium hydroxide, evaporating the solution until it contains 10 per cent moisture and then adding 2-10 per cent of gas tar or pitch. Saponified resins formed by the action of sodium carbonate on sulphite liquor are purified by electrolytic hydrogenation in a 2-compartment cell, the resins being placed in the negative compartment and a 13 per cent sodium carbonate solution in the positive.

The liquid resin obtained in digesting wood to wood pulp is known as tall oil (or tallöl). Fahrion<sup>67</sup> described it as a dark brown, fairly thin oil, soluble in

<sup>60</sup> O. Aschan and K. E. Ekholm, *Finska Kem. Medd.*, 1918; *J.S.C.I.*, 1919, 38, 646A.

<sup>61</sup> F. J. Wallace, British P. 370,752, 1931, to Robeson Process Co.; *Brit. Chem. Abs.*, B, 1932, 614. French P. 719,394, 1931; *Chem. Abs.*, 1932, 26, 3945. German P. 593,505, 1934; *Chem. Abs.*, 1934, 28, 3606.

<sup>62</sup> O. W. Knight, U. S. P. 1,143,174, June 22, 1915; *Chem. Abs.*, 1915, 9, 2318.

<sup>63</sup> A. Schmidt, British P. 178,104, 1922; *J.S.C.I.*, 1923, 42, 765A.

<sup>64</sup> H. Stinnes, German P. 397,604, 1921; *J.S.C.I.*, 1925, 44, 936B.

<sup>65</sup> German P. 468,597, 1927, to Österreichische-Alpine Montanges; *Chem. Abs.*, 1929, 23, 1768.

<sup>66</sup> French P. 619,861, 1925, to L. Petit-Devaucelle; *Brit. Chem. Abs.*, B, 1928, 183.

<sup>67</sup> W. Fahrion, *Z. angew. Chem.*, 1909, 22, 882; *Chem. Abs.*, 1909, 3, 1697. See also H. Bergström, *Papier-Fabr.*, 1912, 10, 251, 359; *Chem. Abs.*, 1912, 6, 2528.

alcohol, ether and acetone. He found that on distillation tall oil gives products similar to those from common rosin.<sup>66</sup> From the results of several investigators<sup>67</sup> the following principal constituents of tall oil are indicated:

Resin acids.....	30-45 per cent
Fatty acids.....	45-60 " "
Unsaponifiable matter....	6-12 " "

The unsaponifiable portion is a yellow viscous oil containing waxy or pitchy material.

Crude tall oil was described by Hübscher<sup>70</sup> as a dark brown, viscous liquid containing a crystalline sediment of abietic acid (4 per cent). From this crude oil a yellow distillate containing 18 per cent unsaponifiable matter was obtained.<sup>71</sup> The calcium soap of tall oil was found to be a viscous, sticky mass insoluble in alcohol, but soluble in benzene. Its use in plasters and flypaper was suggested. Hübscher isolated tall oil pitch as a glassy, brittle mass (melting at 85°C.), soluble in benzene. He suggested it be used for insulation and as an ingredient in cheap grades of black varnish. Wolff<sup>72</sup> found that drying agents harden tall oil so that it forms a brittle film and can be employed as a constituent of paint.

A refined tall oil was produced by Patch and Dambacher<sup>73</sup> by the oxidation of the crude material. Polymerization and condensation also took place during the reaction, which could be carried out either by bubbling oxygen through the oil or by use of compounds which liberated oxygen in the nascent state (e.g., sodium perborate or sodium persulphate). Temperatures of 85-195°C. for 20-50 hours were employed and in some cases iron, aluminum or manganese resinate served as a catalyst. A clear, odorless, dark oil was obtained. This is recommended as a cutting oil or for coating metals, due to its corrosion-retarding properties.

By the fractional vacuum distillation of tall oil, de Keghel<sup>74</sup> effected a separation into fatty acids, resin acids, rosin oil, unsaponifiable matter and pitch. The distilled fatty acids (tallölein) boiling at about 240°C. were suggested for the making of soft soaps, liquid soaps and toilet preparations, and as a base for various greases and oils. The resin fraction (boiling at 290-320°) was described as a brown, resinous, sticky, saponifiable liquid useful in dark-colored printing inks and in axle greases.<sup>75</sup> It was stated that sulphonation of the resin acids yielded a product which can replace Turkey red oil for some purposes.

Another method is that used by Roll<sup>76</sup> in which selective saponification is effected in an organic solvent. The resin soaps form first and can be withdrawn readily from the fatty acid soaps.

Schultze<sup>77</sup> removed the fatty acids from resin acids by an esterification process.

<sup>66</sup> The use of this resin as a substitute for colophony was suggested by P. Klemm (*Chem.-Ztg.*, 1910, 34, 1353; *J.S.C.I.*, 1911, 30, 37).

<sup>67</sup> M. de Keghel, *Rev. chim. ind.*, 1926, 35, 170, 202; *Chem. Abs.*, 1927, 21, 1354. Duesberg, *Seifensieder-Ztg.*, 1925, 52, 873; *Chem. Abs.*, 1926, 20, 514. M. Dittmer, *Z. angew. Chem.*, 1926, 39, 262; *Chem. Abs.*, 1926, 20, 3072. E. Pyhälä, *Chem. Umschau Fette, Öle, Wachse u. Harze*, 1927, 34, 145, 189; *Chem. Abs.*, 1927, 21, 3472. K. Dittler, *Chem.-Ztg.*, 1928, 52, 577; *Chem. Abs.*, 1928, 22, 4238. H. Sandquist, *Z. angew. Chem.*, 1922, 35, 531; *Chem. Abs.*, 1923, 17, 339.

<sup>70</sup> J. Hübscher, *Seifensieder-Ztg.*, 1921, 48, 231; *Chem. Abs.*, 1921, 15, 2177.

<sup>71</sup> See also K. Fricke, *Allgem. Öl-u. Fettztg.*, 1927, 24, 45; *Chem. Abs.*, 1928, 22, 3794.

<sup>72</sup> H. Wolff, *Farben-Ztg.*, 1919, 24, 653; *Chem. Abs.*, 1919, 13, 2289.

<sup>73</sup> R. H. Patch and F. Dambacher, U. S. P. 1,938,532, Dec. 5, 1933, to E. F. Houghton and Company; *Chem. Abs.*, 1934, 28, 1207.

<sup>74</sup> M. de Keghel, *loc. cit.* Cf. W. Schultze, U. S. P. 1,826,224, Oct. 6, 1931; *Chem. Abs.*, 1932, 26, 613. Also British P. 281,637, 1927, to Öl-u. Fette-Chemie G.m.b.H.; *Brit. Chem. Abs. B*, 1929, 254. German P. 477,829, 1926; *Chem. Abs.*, 1929, 23, 4842.

<sup>75</sup> See W. Schmid, *Forben-Chemiker*, 1931, 2, 306; *Chem. Abs.*, 1931, 25, 5582.

<sup>76</sup> R. Roll, German P. 448,960, 1923; *Brit. Chem. Abs. B*, 1923, 60.

<sup>77</sup> W. Schultze, U. S. P. 1,786,802, Nov. 26, 1929; *Chem. Abs.*, 1930, 24, 744. Also British P. 278,697, 1927, to Öl-u. Fett-Chemie G.m.b.H., *Brit. Chem. Abs. B*, 1929, 293. German P. 484,348, 1926; *Chem. Abs.*, 1930, 24, 984.

A mixture of tall oil (100 parts), alcohol (25 parts) and concentrated sulphuric acid (4 parts, specific gravity 1.84) is heated under reflux for two hours, causing esterification of fatty acids but leaving the resin acids unaffected. Sulphuric acid is removed and the ester mixture is treated with caustic soda solution in slight excess of that needed to neutralize the resin acids and the residual sulphuric acid. The mixture is then stirred with benzene, resulting in the formation of two layers, the upper one containing fatty acid esters dissolved in benzene, and the lower one the sodium soaps of resin acids in water-alcohol solution. The layers are separated and the fatty acids and resin acids recovered.

In the method of Franzen and Held<sup>78</sup> the resin and fatty acids were esterified simultaneously with a polyhydric alcohol (e.g., glycerol or ethylene glycol). The resulting mixture was heated with water in the presence of a catalyst, thus hydrolyzing the fatty esters but not the resin acid esters. Free fatty acids were then separated from resin acid esters by steam distillation. In one instance refined tall oil was treated with excess glycerol and a small amount of tin powder. Esterification was complete after 4 hours heating at 230°C. The fatty acids were liberated by heating the mixed esters with water at 180°C. in an autoclave with zinc dust as a catalyst. Still another procedure consists in treating a warmed solution of tall oil in mineral oil with sufficient sulphuric acid to effect separation of resins.<sup>79</sup> Levi<sup>80</sup> removed pitchy material from tall oil by precipitation with petroleum benzene.

By mixing tall oil (2 parts) with glue or gelatin (1 part) and water (1 part) an emulsifying agent for oils or bituminous substances is formed.<sup>81</sup> A core-binding composition for castings is made from the oil blended with a drying oil (linseed oil), a solvent (pine oil) and either dextrin, molasses, glue or starch.<sup>82</sup> The ingredients may be emulsified with an alkali or with cobalt linoleate. Addition of cresols, hydrocarbon oils, or wood tar to tall oil yields a preservative coating for wood.<sup>83</sup> An adhesive for catching insects consists of chlorinated tall oil incorporated with such substances as carnauba wax, castor oil, bleached wax acids and esterified ozokerite.<sup>84</sup>

An emulsifying agent is obtained when tall oil is esterified with an aliphatic polyhydric alcohol (glycerol), using calcium or magnesium glycerate as a catalyst, and the ester is sulphonated with sulphuric acid, oleum or sulphuric acid monohydrate at temperatures below 40°C.<sup>85</sup> Also, sulphonation of other esters or amides<sup>86</sup> derived from this oil, or of a mixture of the oil (100 parts) and phenol (30 parts) gives water-soluble products which may be utilized in the textile industry,<sup>87</sup> for example, as dispersing agents. Partial reduction of tall oil constituents gives aliphatic ketones which may be sulphonated to yield wetting or dispersing agents.<sup>88</sup> Textile oils<sup>89</sup> or cleansing agents are made also by emulsifying tall oil with a fatty acid soap and aniline,<sup>90</sup> or by mixing the oil with vegetable

<sup>78</sup> H. Franzen and R. Held, U. S. P. 1,921,566, Aug. 8, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5207. German P. 578,843, 1933; *Chem. Abs.*, 1934, 28, 922.  
<sup>79</sup> German P. 434,924, to Chem. Fabr. Florsheim H. Noerdlinger A.-G.; *Brit. Chem. Abs.* B 1927, 258.

<sup>80</sup> R. Levi, German P. 424,031, 1924; *Kunststoffe*, 1926, 16, 178.

<sup>81</sup> J. H. Disney and J. C. Kernot, British P. 274,142, 1926; *Brit. Chem. Abs.* B, 1927, 755.

<sup>82</sup> H. M. Bunbury, British P. 348,315, 1930, to Imperial Chem. Industries, Ltd.; *Chem. Abs.*, 1932, 26, 3081.

<sup>83</sup> N. A. Alexander, British P. 229,296, 1924; *Chem. Abs.*, 1925, 19, 354.

<sup>84</sup> British P. 306,906, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 5286.

<sup>85</sup> H. M. Bunbury and R. P. McGivern, British P. 369,985, 1930; *Chem. Abs.*, 1933, 27, 3046.

<sup>86</sup> British P. 340,272, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4136.

<sup>87</sup> Swiss P. 156,113, 1931, to J. R. Geigy A.-G.; *Chem. Abs.*, 1933, 27, 1212.

<sup>88</sup> British P. 343,098, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1931, 579.

<sup>89</sup> Oils for textiles were made by hydrogenating tall oil in the process of M. Melamid (British P. 169,962 and 170,562, 1921; *J.S.C.I.*, 1923, 42, 22A).

<sup>90</sup> German P. 479,085, 1925, to Hein & Compagnie; *Chem. Abs.*, 1929, 23, 4842.

oils and heating the mixture *in vacuo*, treating with superheated steam, and then allowing the liquid to cool in an inert atmosphere.<sup>91</sup>

Grohn<sup>92</sup> prepared coating compositions by dissolving in benzene (or a similar solvent) the esters derived from tall oil and polyhydric alcohols or phenols. Drying oils, pigments and driers can be added if necessary. A sizing composition for paper consists of ordinary rosin size incorporated with not more than 30 per cent of refined tall oil resin. This procedure lowers the melting point of the composition.<sup>93</sup>

Plastic masses for electrical or heat-insulation are made by mixing the distillation residues of tall oil, or of natural resins, with sulphur, heating the mixture until it becomes ropy, and then incorporating it with fillers (e.g., asbestos) and the condensation products of acetylene or of aldehydes, e.g., phenol-formaldehyde.<sup>94</sup>

### RESINS FROM CARBOHYDRATES

Although many of the products mentioned in this section can be considered modifications of synthetic resins discussed elsewhere in the text (e.g., phenol-aldehyde and urea-aldehyde resins), they are grouped together because of the convenience of classification. Since in this work classification is primarily one of starting materials, those resins derived from carbohydrates, viz., plant materials, are assembled here. Carbohydrates are aldehyde-alcohols, ketone-alcohols or compounds which are converted by hydrolysis into aldehyde-alcohols or ketone-alcohols. Formaldehyde has been polymerized to carbohydrates by the action of bases.<sup>95</sup> Carbohydrates would be expected, therefore, to be convenient and cheap sources for the production of synthetic resins by reaction with urea or phenol.<sup>96</sup>

Resins said to be suited for molding or forming into sheets and films were made by Ford<sup>97</sup> by the condensation of saccharides with aldehydes and urea.<sup>98</sup> When sucrose was used as the saccharide the product was colorless and transparent. The employment of molasses and cane sugar resulted in dark resins. As an example cane sugar (300 parts) is dissolved in 36 per cent formalin solution (250 parts) and the mixture is heated gently (100-105°C.) until all reaction ceases. Then the liquid is heated to boiling and a small amount of hexamethylenetetramine (10 parts) is added. Boiling is continued and urea (75 parts) is introduced in small quantities at a time. When all the urea has reacted, the viscous material is immediately poured into molds and allowed to harden in the air.

A resin with different characteristics is obtained if phthalic anhydride is used instead of urea.<sup>99</sup> Reaction is carried out as described above until after the hexamethylenetetramine has been added. The mixture is heated to 180°C. and then phthalic anhydride (300 parts) is added in small portions. When reaction is complete the mass is cooled to 90°C. and maintained there for several hours to remove water. The liquid is poured into molds to cool, yielding a water-white, non-resilient substance. It is somewhat brittle, giving a sharp fracture, and is soluble in ace-

<sup>91</sup> German P. 485,944, 1923, to Continentale A.-G. für Chemie & Reichverkehrsbanke G.m.b.H.; *Chem. Abs.*, 1930, 24, 1241

<sup>92</sup> H. Grohn, German P. 526,491, 1928, to Firma Ewald Dörken; *Chem. Abs.*, 1931, 25, 4725.

<sup>93</sup> E. J. Johnstone, U. S. P. 1,929,115, Oct. 3, 1933, *Chem. Abs.*, 1933, 27, 5978.

<sup>94</sup> German P. 455,551, 1923, and its addition 471,835, 1924, to Smit A.-G.; *Brit. Chem. Abs. B.*, 1930, 157, *Chem. Abs.*, 1929, 23, 2540

<sup>95</sup> See O. Loew, *Ber.*, 1888, 21, 270. H. Schmalfuss and K. Kalle, *Ber.*, 1924, 57, 2101; *Chem. Abs.*, 1925, 19, 1403. H. Schmalfuss, *Biochem. Z.*, 1927, 185, 70; *Brit. Chem. Abs. A.*, 1927, 648

<sup>96</sup> A short summary of carbohydrate resins is given by J. Pokorný, *Kunststoffe*, 1927, 17, 31; *Plastics*, 1927, 3, 158.

<sup>97</sup> A. S. Ford, U. S. P. 1,949,831, Mar. 6, 1934, to Industrial Sugar Products Corp.; *Chem. Abs.*, 1934, 28, 3255.

<sup>98</sup> Resins of this type have the trade name Sakaloid. See A. S. Ford, *Plastics*, 1931, 7, 448; *Chem. Abs.*, 1931, 25, 5308.

<sup>99</sup> A. S. Ford, U. S. P. 1,949,832, Mar. 6, 1934, to Industrial Sugar Products Corp.; *Chem. Abs.*, 1934, 28, 3255.

tone and similar solvents. If moisture is removed by heating at temperatures higher than 90°C. the products will range in color from light yellow to jet black, depending on conditions. The black color is obtained by heating at 250°C. for 10 hours. The phthalic anhydride resin can be pulverized and mixed with inert bodies (e.g., powdered glass wool), synthetic or natural resins, cellulose derivatives, drying oils or reclaimed rubber or it may be dissolved in ether, acetone, amyl acetate or toluene for use as a varnish.

The employment of phthalic acid in place of the anhydride as well as the use of tartaric, malic and similar aliphatic acids yielded clear, water-white bodies with the same general characteristics.<sup>100</sup>

A variation of this method<sup>101</sup> involves reacting urea directly with a carbohydrate (e.g., cornstarch), using 50 per cent sulphuric acid to assist condensation. A methylene hardening agent is then added and the final product obtained by heating.

Hawerlander<sup>102</sup> has hardened sugar-formaldehyde resins either by heating or by exposure to the atmosphere. For instance, brown cane sugar is dissolved in twice its weight of 40 per cent formaldehyde and the solution is heated at 40°C. for 10 minutes. The resulting liquid is then ready to be used as a binder in making molded articles from fibrous material. The solution will set within 24-48 hours in the air or in 6-10 minutes at 200°C., yielding a hard, plastic material. Setting may be accelerated by adding about 2 per cent (of the weight of sugar) of sodium sulphite to the reaction mixture. Plastic masses are formed also by the condensation of formaldehyde with starch, using as accelerators various organic acids together with a small amount of an inorganic acid<sup>103</sup> (e.g., sulphuric acid with lactic acid or phthalic anhydride).

A textile finish<sup>104</sup> is obtained from starch by condensing it with an aldehyde or with hexamethylenetetramine while cold. When used to treat fabrics and dried in a slightly acidic condition, resistance to washing is secured.

Meigs<sup>105</sup> has described the condensation of carbohydrates with phenols, amines and organic acids. The products are black in color, water-insoluble and said to be useful in baking-type lacquers and molding compositions. The following is an example of the reaction between carbohydrates and organic acids: Glucose (126 parts), dextrin (54 parts), salicylic acid (138 parts), aniline (20 parts) and water (100 parts) are mixed together and refluxed for 45 minutes, yielding a black, resilient mass. For treatment with amines one procedure is to reflux for 2 hours a mixture of glucose (360 parts), aniline (150 parts), water (125 parts) and oxalic acid (5 parts), forming a semi-solid material which becomes infusible when heated above 125°C.

To effect combination of carbohydrates and phenols, a mixture, for example, of glucose (360 parts), phenol (170 parts), water (200 parts), aniline (30 parts) and oxalic acid (4 parts) is heated under reflux for 3.5 hours yielding a black resin (360 parts) which can be hardened by the addition of 5 per cent of hexamethylenetetramine and heating to 160°C.

Sucrose<sup>106</sup> also condenses with phenol, with either mineral or organic acids as cata-

<sup>100</sup> A. S. Ford, U. S. P. 1,974,064, Sept. 18, 1934, to Industrial Sugar Products Corp.; *Chem. Abs.*, 1934, 28, 7044.

<sup>101</sup> British P. 209,697, 1922, to J. S. Stokes; *J.S.C.I.*, 1924, 43, 224B. See also British P. 208,193, 1922; *J.S.C.I.*, 1924, 43, 141B.

<sup>102</sup> A. Hawerlander, U. S. P. 1,837,216, Dec. 22, 1931, to Halzite Corp.; *Chem. Abs.*, 1932, 26, 1412.

<sup>103</sup> German P. 507,997, 1927, to "Herold" A.-G.; *Chem. Abs.*, 1931, 25, 784.

<sup>104</sup> British P. 414,576, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.* 1934, 880.

<sup>105</sup> J. V. Meigs, U. S. P. 1,801,052 and 1,801,053, April 14, 1931, to Meigsoid Corp.; *Chem. Abs.*, 1931, 25, 3503. See British P. 274,146, 1926, and German P. 529,323, 1927; *Chem. Abs.*, 1928, 22, 2072; 1931, 25, 5050.

<sup>106</sup> J. V. Meigs, U. S. P. 1,845,314, Feb. 16, 1932, to Meigsoid Corp. This application and the application for U. S. P. 1,832,038, Nov. 17, 1931, were involved in interference with applications of McIntosh corresponding to U. S. P. 1,753,030, April 1, 1930, and 1,820,816, Aug. 25, 1931, to Continental Diamond Fibre Co.

lysts, to form a black, almost tarry mass which can be hardened by heat or exposure to air, as well as by use of a variety of condensing agents including acids, bases, salts and benzyl chloride.<sup>107</sup> Phenol (600 parts) and 500 parts of a sugar containing 84 per cent dextrose are heated with 5 parts of sulphuric acid, the water being removed through a fractionating column as fast as it is formed.<sup>108</sup> Excess phenol is removed by vacuum distillation. The black resin secured by the apparent interaction of 1 mol of dextrose and 2 mols of phenol melts to a viscous liquid which may be hardened by heating to 140°C. with 3-10 per cent of hexamethylenetetramine. Other materials (e.g., furfural and aniline, the naphthols, glycerol and naphthylamines) may be used instead of phenol. It has been stated that greater proportions of hexamethylenetetramine (10-20 per cent of the weight of phenol-carbohydrate) tend to increase the mechanical strength of molded objects made from these resins.

It was reported by Meigs<sup>109</sup> that the properties of phenol-carbohydrate resins are modified by certain fillers usually employed in molding compositions. The more difficultly water-soluble metallic bases in particular are said to improve electrical properties of molded articles. It is considered that these bases react with other constituents of the resin, probably with decomposition of water-soluble substances. Insulation resistance is reported to be increased ten-fold by the incorporation of about 10 per cent of calcium hydroxide.<sup>110</sup> The usual procedure is to add the metallic compound to the fusible carbohydrate-phenol resin, together with a hardening agent, followed by hot-molding at 150-180°C. Another method<sup>111</sup> involves the use of fatty oils, or pitches from the distillation of these oils. For example, 960 g. phenol, 400 g. corn sugar (85 per cent dextrose), 240 g. tung oil and 13.6 g. concentrated sulphuric acid were heated at 180-190°C. until most of the water was removed. Apparently the oil took part in the condensation, since the reaction product, a reddish-brown mass, dissolved completely in alcohol, which is not a solvent for tung oil.

A dark, viscous body was obtained by McIntosh<sup>112</sup> by heating equal parts of starch, phenol and water, with sulphuric acid as a catalyst, for several hours under reflux. This material was soluble in acetone, alcohol and benzene and consequently was suggested as a varnish base. Hardening was attained by heating at 125°C. for 10-12 hours, the reaction being accelerated by pressure and by addition of hexamethylenetetramine, benzidine-acetone or sodium-acetone-bisulphite. The ultimate product was hard, infusible and insoluble in most solvents. By impregnating fibrous or porous material with a resin of intermediate stage and molding in laminated form, a composition useful in making gears, insulators and sound-records was secured. The final resin was improved by removing or neutralizing the catalyst after the initial condensation. Modifications in the method include substitution of sugars or of other carbohydrates for starch as well as the use of other phenols and the employment of pyridine, aniline hydrochloride or sulphur monochloride as catalysts.

The use of catalysts, especially mineral acids, in condensations of carbohydrates and phenols has the disadvantage of introducing in the resin substances which increase moisture-absorption, decrease electrical strength and corrode metal dies during molding. Moreover, these undesirable features are difficult to eliminate. By carrying out the reaction between starches or sugars and phenols in a closed vessel

<sup>107</sup> J. V. Meigs, U. S. P. 1,832,038, Nov. 17, 1931, to Meigsoid Corp.; *Chem. Abs.*, 1932, 26, 3622.

<sup>108</sup> J. V. Meigs, U. S. P. 1,593,342, July 20, 1926; *Chem. Abs.*, 1926, 20, 3242. British P. 274,146, 1926; *Chem. Abs.*, 1928, 22, 2072. German P. 529,323, 1926; *Chem. Abs.*, 1931, 25, 5050.

<sup>109</sup> J. V. Meigs, U. S. P. 1,877,417, Sept. 13, 1932, to Plastix Corp.; *Chem. Abs.*, 1933, 27, 200. Also U. S. P. 1,975,471, Oct. 2, 1934; *Chem. Abs.*, 1934, 28, 7563.

<sup>110</sup> J. V. Meigs, U. S. P. 1,993,708, Mar. 8, 1935, to Plastix Corp.; *Chem. Abs.*, 1935, 29, 2628.

<sup>111</sup> J. V. Meigs, U. S. P. 1,868,215 and 1,868,216, July 19, 1932, to Plastix Corp.; *Chem. Abs.*, 1932, 26, 5221. See also Chapter 24.

<sup>112</sup> J. McIntosh, U. S. P. 1,753,030, April 1, 1930, and 1,820,816, Aug. 25, 1931, to Continental Diamond Fibre Co.; *Chem. Abs.*, 1930, 24, 2624; 1931, 25, 5790. British P. 231,553, 1923; *Chem. Abs.*, 1925, 19, 903.

at 200-260°C., Novotny and Romieux<sup>113</sup> succeeded in condensing these materials without a catalyst. The pressure generated during the reaction, as well as the high temperature, facilitated the process. A brownish-black, hard lustrous resin was obtained by heating 100 pounds of corn starch and 150 pounds of phenol in a pressure kettle at 250°C. for 2-3 hours and then removing uncombined phenol by distillation. The product may be more fully cured by additional heating and by use of the usual aldehyde type of accelerators. Urea has been suggested as a substitute for phenol.<sup>114</sup>

Konther<sup>115</sup> suggests that phenol-carbohydrate resins, after washing with water, be dissolved in methyl or ethyl alcohol to give a black enamel varnish which is resistant to heat. As a modification, 20 parts of rubber are dissolved in the resin by the application of heat and pressure.<sup>116</sup>

Phenol, formaldehyde and a carbohydrate were condensed with an alkaline catalyst by Loetscher<sup>117</sup> to a sufficient degree only to form a water-soluble resin, which could be used in aqueous solution for laminated or veneered articles, or dried and admixed with wood flour for molding purposes. One such product is secured by heating phenol, 40 per cent formaldehyde and a 50 per cent cane sugar syrup in equal parts at 93-108°C. with about 2 per cent of dilute sodium or potassium hydroxide solution. The reaction is stopped just before the resin reaches its water-insoluble state. When starch is substituted for cane sugar, much larger quantities of water and caustic alkali are required.

The resistance of fusible phenol-carbohydrate resins to ammonia and to water was improved by Meigs<sup>118</sup> by a heat-treatment at 240-270°C. for 2-3 hours in a high-boiling solvent (b.p. 270-300°C.). The resultant compound is firm and hard, yet fusible enough for molding or milling on hot rolls and soluble in alcohol, acetone and benzene. In one instance, 800 g. of the intermediate substance were heated with 190 g. of creosote oil residue (b.p. over 300°C.). The resin obtained was mixed with wood flour and hexamethylenetetramine and cured in a mold at 120°C., to yield a glossy, moisture-resistant material.

An alcohol-soluble body was produced by Bau<sup>119</sup> by condensing formaldehyde, a phenol and an aldose (e.g., glucose) in the presence of hydrochloric acid at 65-70°C. According to Bau, the hydroxybenzyl alcohol resulting from the interaction of phenol and formaldehyde forms a glucoside, and subsequent polymerization takes place.

Hard infusible products were made by Tarassov<sup>120</sup> by the condensation of wheat starch, potato flour or potato molasses with formaldehyde, a phenol and a sulphonated hydrocarbon (e.g., naphtha sulphonic acids).

Meigs also obtained resins from carbohydrates and polyhydric alcohols.<sup>120</sup> In this procedure a small amount of a mineral acid is used and presumably decomposes the carbohydrate into humic acid derivatives which then combine with the alcohol to form a resin. Reaction takes place in a vessel equipped with a reflux condenser maintained at such a temperature that water vapor will escape but alcohol vapors will be condensed to return to the reaction vessel. To 400 parts of glycerol at 100°C. are added 6 parts of sulphuric acid (sp.gr. 1.84), followed by 400 parts of corn sugar (crude

<sup>113</sup> E. E. Novotny and C. J. Romieux, U. S. P. 1,815,930, July 28, 1931, to J. S. Stokes; *Chem. Abs.*, 1931, 25, 5481. Cf. E. E. Novotny and C. J. Romieux, U. S. P. 1,721,315, July 16, 1929, to J. S. Stokes; *Chem. Abs.*, 1929, 23, 4367.

<sup>114</sup> British P. 209,697, 1922, to J. S. Stokes; *J.S.C.I.*, 1924, 43, 224B.

<sup>115</sup> F. Konther, German P. 380,764, 1921; *J.S.C.I.*, 1923, 42, 1186A.

<sup>116</sup> F. Konther, German P. 402,541, 1923; *J.S.C.I.*, 1925, 44, 17B.

<sup>117</sup> E. C. Loetscher, U. S. P. 1,959,433, May 22, 1934; *Chem. Abs.*, 1934, 28, 4616.

<sup>118</sup> J. V. Meigs, U. S. P. 1,923,321, Aug. 22, 1933, to Plastix Corp.; *Chem. Abs.*, 1933, 27, 5203.

<sup>119</sup> A. Bau, British P. 218,954, 1923; *Chem. Abs.*, 1925, 19, 581.

<sup>120</sup> K. Tarassov, British P. 102,751, 1916; *Chem. Abs.*, 1917, 11, 1027. British P. 171,729, 1920, to H. Renner & Co.; *J.S.C.I.*, 1922, 41, 60A.

<sup>120</sup> J. V. Meigs, U. S. P. 1,908,485, May 9, 1933, to Sweets Laboratories, Inc.; *Chem. Abs.*, 1933, 27, 3759.



dextrose) and the mixture is heated for 4 hours at 190-230°C. The reaction product is washed with hot water and then dried at 100°C. yielding a dark brown, glossy, thermoplastic mass, which can be mixed with fillers for the preparation of molded articles. The resin is made infusible by heating it for about 1 hour at 130-160°C. A modification of this method<sup>121</sup> is to digest a carbohydrate, e.g., dextrose, molasses, starch or levulose, with caustic soda to form sodium salts of organic hydroxy acids, after which butyl alcohol, glycerol, diethylene glycol or other alcohols are added, together with hydrochloric acid. The latter liberates the organic acids from their salts and acts as a catalyst to bring about a reaction between these acids and the alcohol. Resinous substances are formed, compatible with cellulose compounds and soluble in ethyl and butyl acetate or other esters and in alcohols. The product may be purified by washing with water to remove salts, or by extraction with alcohol.

Light-colored, resinous bodies are said to be formed by the condensation of cyclic ketones with carbohydrates and with polyhydric alcohols (other than a polyvinyl alcohol) containing at least 6 carbon atoms.<sup>122</sup> (With some of the reagents the products are crystalline.) In one case, 100 parts of sucrose are suspended in 100 parts of methyl alcohol to which 0.25-0.5 per cent of concentrated sulphuric acid has been added. The sugar is dissolved by heating under reflux on a water bath. The solution is cooled and 300-400 parts of 2-methylcyclohexanone and 40 parts of concentrated sulphuric acid are added. This mixture is agitated at 0-5°C. for 4 hours and then neutralized with sodium carbonate. After the removal of excess methylcyclohexanone there is obtained a solid, transparent resin which is soluble in many organic solvents but only slightly in benzene.

Weiss<sup>122a</sup> produced a water-soluble resin by reacting dextrose with acid anhydrides. Thus 50 parts of maleic anhydride and 75 parts of phthalic anhydride are heated with 180 parts of dextrose at 150°C. Further heating tends to reduce the solubility.

Sucrose and other carbohydrates when heated with persulphates yield hard, insoluble and infusible oxidation products according to Böhrer.<sup>123</sup> E.g., 50 parts of crude sugar are dissolved in 50 parts of alcohol (50 per cent) and treated with 3 parts of ammonium persulphate. The solution is evaporated and the residue heated to 180°C. yielding a water-insoluble mass. The hardness and elasticity of the resin are modified by the addition of oils or other resins to the above solution before evaporation. The material can be mixed with fillers to make molded products.

The action of phloroglucinol on sugars without the application of heat was studied by Fischer and Jennings<sup>124</sup> but they did not succeed in isolating any stable substances. Counciler<sup>125</sup> obtained condensation products of phloroglucinol with various aldehydes and sugars (e.g., with acetaldehyde, dextrose, mannose, galactose, levulose and arabinose). A solution of 6 g. of dextrose and 5.4 g. of phloroglucinol in 30 cc. of water, on treatment with hydrogen chloride gas, slowly thickened and turned reddish-brown. The product, when purified, was an amorphous yellow-green to olive-green precipitate. It was almost insoluble in water, ether and benzene, but dissolved in alcohol. Heated to 200°C. it carbonized but was non-combustible. The analysis gave its empirical formula as  $C_{12}H_{10}O_8$ , which represents the condensation of 1 mol of dextrose and 1 mol of phloroglucinol with the elimination of 3 mols of water. Other results are shown in Table 36.

Resinous substances were also obtained by Counciler<sup>126</sup> from phloroglucinol and formaldehyde, acetaldehyde, propionaldehyde and isobutyraldehyde.

<sup>121</sup> J. V. Meigs, U. S. P. 1,982,822, Dec. 4, 1934, to Sweets Laboratories, Inc.; *Chem. Abs.*, 1935, 29, 626.

<sup>122</sup> British P. 385,139, 1932, to I. G. Faibennnd A.-G.; *Chem. Abs.*, 1933, 27, 4247.

<sup>122a</sup> J. M. Weiss, U. S. P. 1,990,380, Apr. 30, 1935, to Weiss & Downs, Inc.

<sup>123</sup> C. Böhrer, German P. 552,380, 1929; *Chem. Abs.*, 1932, 26, 4426.

<sup>124</sup> E. Fischer and W. L. Jennings, *Ber.*, 1894, 27, 1855.

<sup>125</sup> C. Counciler, *Ber.*, 1895, 28, 24; *Chem.-Ztg.*, 1894, 18, 1617; *Chem. Zentr.*, 1894, 2, 844.

<sup>126</sup> C. Counciler, *Chem.-Ztg.*, 1896, 20, 585, 599; *Ber.*, 1897, 30, 990R.

TABLE 36.—*Phloroglucinol-Sugar Condensations.*

Sugar	Mols Sugar	Mols Phloroglucinol	Mols H <sub>2</sub> O Eliminated
Arabinose.....	3	3	6
Xylose.....	3	3	6
Galactose.....	3	3	8
Dextrose.....	3	3	9
Levulose.....	3	3	10

Various processes for the utilization of hulls and spent glutes have been devised. Gluten and waste from starch works, for instance, can be kneaded with phenolic materials which form an insoluble compound with the vegetable proteins, according to Basset.<sup>127</sup> The paste of gluten and phenol may be used for the manufacture of plastic substances or treated with acetone or a similar solvent to separate the gluten from the phenol. Preparation of resins from spent grains or malt is also described by Basset.<sup>128</sup> These materials are condensed with phenolic bodies using sodium hydroxide, zinc chloride or sodium zincate as a catalyst. Formaldehyde may also be used in the operation. The resulting resin has been suggested for thermal and electrical insulation. Resinous material soluble in organic solvents was prepared by Tzonev and Yavnel<sup>129</sup> by heating the hulls of sunflower seeds at over 100°C. with phenol and a mineral acid catalyst. The reaction was assumed to be a condensation of phenol with furfural, glucose, xylose and other products of hydrolysis.

A distinction is made by Maksarov and Andrianov<sup>130</sup> between resinous starch esters, which they term semi-synthetic resins, made from pure starch, and the benzylated derivatives of starchy substances such as potatoes, flour and bran. The latter contain proteins, amino acids and other analogous compounds in addition to carbohydrates and form condensation products, which are considered to be true resins and are classifiable as "benzylamylonic esters."

Molasses and molasses residues are suggested as a source of non-sugar organic matter capable of conversion into hard, heat-resistant resins for making bricks and tiles. According to Vazquez<sup>131</sup> the molasses is extracted with a mixture of sulphuric acid, alcohol and organic solvents (e.g., chlorinated hydrocarbons) which do not dissolve sugar. After stirring at 25-30°C. until the mass is uniform, a dark liquor is allowed to separate. This contains the solvents and organic salts and other impurities from the molasses. On evaporation, a residue is left which solidifies on cooling and hardens at 100°C. or higher to an insoluble, infusible resin, which may be ground and used with a binder for molding. If the liquor from the extraction operation is concentrated to a thick syrup it can serve as a binding agent for the hardened product. The mixture is adaptable for cold molding followed by baking at gradually rising temperatures to 250°C.

Methods for the preparation of resinous condensation products of pectous matter obtained from plants have been devised by Hawerlander.<sup>132</sup> The non-fibrous constituents of cereal straws, plant stalks and grasses are obtained by agitating the plant material with water or steam. The aqueous solution of non-fibrous substances is removed by pressing the fibers and is then evaporated, yielding the pectous residue as a dark brown, viscous mass. This is mixed with an equal volume of 40 per cent formaldehyde and the mixture thoroughly agitated. The temperature is raised to 30°C. and small quantities of sodium sulphite (or other

<sup>127</sup> P. E. Basset, French P. 676,671, 1928; *Chem. Abs.*, 1930, 24, 3128.

<sup>128</sup> P. E. Basset, French P. 649,152, 1927; *Chem. Abs.*, 1929, 23, 2772. British P. 293,436, 1927; *Chem. Abs.*, 1929, 23, 1703.

<sup>129</sup> N. Tzonev and N. Yavnel, *Masloboino Zhirouoe Delo*, 1931, (11), 22; *Chem. Abs.*, 1932, 26, 4498.

<sup>130</sup> E. V. Maksarov and K. A. Andrianov, *Plast. Massy*, 1933 (6), 1; *Chem. Abs.*, 1934, 28, 7041.

<sup>131</sup> E. A. Vazquez, U. S. P. 1,976,590, Oct. 9, 1934; *Chem. Abs.*, 1934, 28, 7444.

<sup>132</sup> A. Hawerlander, U. S. P. 1,941,349 and 1,941,350, Dec. 26, 1933, to Albert D. Stewart; *Chem. Abs.*, 1934, 28, 1484, 1536.

condensing agent) are added from time to time until the amount used equals about 1 per cent of the volume of reactants. External heating is not necessary because of the exothermic nature of the reaction. When the mixture has attained a temperature of 70°C. it is cooled to about 25°C. The product is fusible and water-soluble but becomes insoluble on exposure to air. The material can be mixed with fillers and fibers and molded; heat and pressure rendering it infusible.

Hawerlander produced a resin possessing many of the characteristics of phenol-formaldehyde compounds by condensing pectose with an aldehyde and a ketone.<sup>122</sup> This resin, which he terms a pectose resin, is clear and amber-like, melting at 70°C.

As an example of the preparation of such a resin, equal parts of pectous residue (mentioned above), formaldehyde (36-40 per cent) and dimethyl ketone are mixed together and stirred for 6 hours at 35°C. Caustic potash is added during this treatment. When the liquid is subsequently allowed to settle three layers form, the top containing the fat and wax constituents, the bottom a residue and the middle (85 per cent of the total) the desired reaction mixture. The middle layer is removed and treated further with caustic potash, yielding a gummy liquid which solidifies when neutralized with dilute nitric acid. Evaporation of volatile liquids yields a residue of clear amber-like resin. This can be used in lacquers and in molded materials. It is made infusible and insoluble by heating with a hardening agent (e.g., hexamethylenetetramine).

The possibility of the commercial production of xylose from cottonseed hulls<sup>124</sup> led to investigations on the formation of varnish resins from this sugar.<sup>125</sup> Equimolecular proportions of xylose and aniline (150 parts and 92 parts, respectively) when heated at 75-80°C. for 10 minutes yield a clear red resin soluble in acetone. The solution is said to give on wood a varnish resistant to hot water, alkalies and acids (except nitric).<sup>126</sup> The varnish can be made more cheaply by using impure cake-xylose and aniline oil.<sup>127</sup>

It was observed that methylated xylan (by action of methyl sulphate in alkaline solution) tends to form gummy products.<sup>128</sup> The mono-allyl ethers of corn and potato starches and of dextrin and inulin have been described as gummy substances.<sup>129</sup> Sucrose octa-acetate (obtained from sucrose, sodium acetate and acetic anhydride) possesses a crystalline form, but when fused (melting point 69°C.) and cooled it changes to a clear, transparent glass suggesting its use in resins and plastics.<sup>130</sup> Condensation of dulcitol,  $C_6H_{12}O_6$ , with o-nitrobenzaldehyde yields 1,2,5,6-bis(o-nitrobenzylidene)dulcitol, which when isomerized by the action of light, produces a resin.<sup>131</sup>

Hashitani<sup>132</sup> reports that some derivatives of yeast-gum are amorphous or resinous in character. Thus, benzoyl yeast-gum,  $C_6H_5O_5(C_6H_5CO)_3$ , is a whitish, amorphous material, soluble in pyridine and melting at 223-225°C. Depolymerization of yeast-gum with glycerol at 210-220°C. for 4-5 hours gave a substance,  $\alpha$ -yeast-gum, which was white, amorphous, hygroscopic and soluble in water.

<sup>122</sup> A. Hawerlander, U. S. P. 1,941,351 and 1,941,352, Dec. 26, 1933, to Albert D. Stewart; *Chem. Abs.*, 1934, 28, 1559.

<sup>124</sup> W. T. Schreiber, N. V. Geib, B. Wingfield and S. F. Acree, *Ind. Eng. Chem.*, 1930, 22, 497.

<sup>125</sup> J. P. Montgomery, *Ind. Eng. Chem.*, 1931, 23, 761.

<sup>126</sup> However, H. A. Gardner (*Circ., Am. Paint and Varnish Mfrs. Assoc.*, 1932, 410, 170, 411, 169; *Brit. Chem. Abs.* B, 1933, 78; *Chem. Abs.*, 1932, 26, 3938) found that a coating of xylose-aniline resin on maple failed after 1 week exposure.

<sup>127</sup> The cost of this varnish was estimated by Montgomery (*loc. cit.*) at \$1.00 per gallon.

<sup>128</sup> H. A. Hampton, W. N. Haworth and E. L. Hirst, *J.C.S.*, 1929, 1739.

<sup>129</sup> C. G. Tomecko and R. Adams, *J.A.C.S.*, 1923, 45, 2700.

<sup>130</sup> G. J. Cox, J. H. Ferguson and M. L. Dodds, *Ind. Eng. Chem.*, 1933, 25, 969. Sucrose octa-acetate is manufactured by the Niacet Chem. Co., Niagara Falls, N. Y.

<sup>131</sup> I. Tanssescu and E. Macovski, *Bull. soc. chim.*, 1933, 53, 1097; *Chem. Abs.*, 1934, 28, 1330.

<sup>132</sup> Y. Hashitani, *Bull. Agr., Chem. Soc. (Japan)*, 1927, 3, 2; *Chem. Abs.*, 1928, 22, 1141.

## Chapter 37

### Hardened Rosin. Resinates

Among the natural resins the most important is common rosin or colophony obtained from various species of pine trees. Until the advent of tung oil varnishes,<sup>1</sup> rosin was much despised as a natural resin because of the harmful effect produced by its acidic constituents. The present discussion deals with the disadvantages of rosin in its natural state and presents many of the attempts made to convert the resin into a more useful material. The melting point of rosin averages about 80°C., the acid number about 160 and the saponification number about 165.<sup>2</sup>

The amount of gum rosin produced yearly in the United States is at least 300,000-325,000 tons and of wood rosin is about 100,000 tons.<sup>3</sup> Gum rosin is obtained as the residue in the separation of spirit of turpentine from crude turpentine pitch by distillation and wood rosin is procured by naphtha extraction of waste pine-wood after it has been steam distilled to recover pine oil and turpentine.<sup>4</sup> The principal uses for rosin are in the paper, soap<sup>5</sup> and paint and varnish industries.<sup>6</sup> Of growing importance are its uses in modified synthetic resins, adhesives, emulsifiers, waterproofing material and dehairing preparations. Although rosin is a natural resin it is rarely used directly (because of its acid nature) but is converted into soaps or esters.<sup>8</sup> The fact that it is usually made into a modified product justifies the consideration of rosin in a work on synthetic resins.

#### ABIETIC ACID

The principal constituents of American rosin are abietic acid (more than 90 per cent) and a small amount of non-acid material called resene.<sup>9</sup> Considerable work has been done on the determination of the structure of abietic acid. Ruzicka and his co-workers<sup>10</sup> give as the structure the following:

<sup>1</sup> See Chapters 28-29.

<sup>2</sup> The physical properties of wood rosin have been studied by J. M. Peterson, *Ind. Eng. Chem.*, 1932, 24, 168. A comparison of French and American gum rosins was made by A. R. Hitch, *Ind. Eng. Chem.*, 1931, 23, 1185. For a discussion of wood rosin and gum rosin see A. Zinoviev, *Masloboino Zhirovoe Delo*, 1928 (10), 24; *Chem. Zentr.*, 1929, 1, 3040. A study of the viscosity-temperature relationship of molten rosin is given by J. M. Peterson and E. Fragoff, Jr., *Ind. Eng. Chem.*, 1932, 24, 173. See also H. E. Nash, *ibid.*, 177.

<sup>3</sup> O. Wilson, *Ind. Eng. Chem. News Ed.*, 1934, 12, 170. The estimated world production of rosin is 600,000 tons. The paper industry absorbs 38 per cent, the soap trade 24 per cent and the varnish industries 21 per cent of this amount. See A. J. Gibson, *J.S.C.I.*, 1934, 53, 989.

<sup>4</sup> See R. C. Palmer, *Ind. Eng. Chem.*, 1934, 26, 703.

<sup>5</sup> See A. Campbell, *Ind. Eng. Chem.*, 1934, 26, 718.

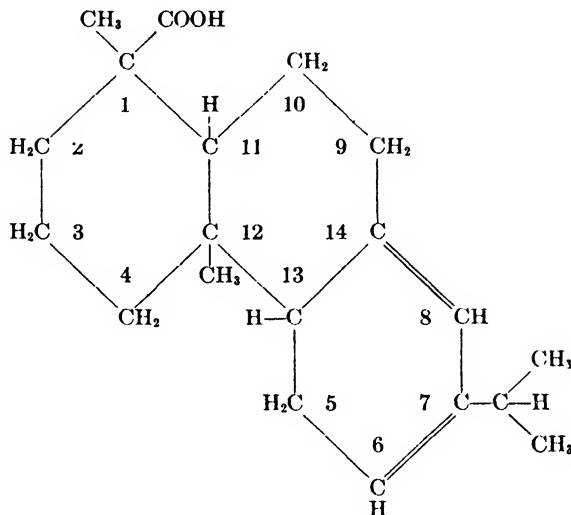
<sup>6</sup> J. McE. Sanderson, *Ind. Eng. Chem.*, 1934, 26, 711. See also F. W. Hopkins, *Am. Paint J.*, 1930, 14 (38), 68; *Chem. Abs.*, 1930, 24, 4409.

<sup>7</sup> O. A. Pickett and J. M. Schantz, *Ind. Eng. Chem.*, 1934, 26, 707.

<sup>8</sup> Rosin esters are considered in Chapter 38.

<sup>9</sup> For some of the analyses of rosin see E. Stock, *Farben-Ztg.*, 1921, 27, 156, *et seq.*; *Chem. Abs.*, 1922, 16, 504. L. P. Zhereboff, *Bumazhnaia Prom. (Russia)*, 1923, 2 (1), 59; *Chem. Abs.*, 1924, 18, 1197. E. Knecht and N. B. Maurice, *J. Soc. Dyers Colourists*, 1925, 41, 356; *Chem. Abs.*, 1926, 20, 299. D. N. Shaw and L. B. Sebrell, *Ind. Eng. Chem.*, 1926, 18, 612. A study of color tests for abietic acid was made by W. A. LaLande, Jr., *J.A.C.S.*, 1933, 55, 1536.

<sup>10</sup> L. Ruzicka, P. J. Ankersmit and B. Frank, *Helv. Chim. Acta*, 1932, 15, 1289; *Brit. Chem. Abs. A.*, 1932, 1254. L. Ruzicka, H. Waldmann, P. J. Meier and H. Hösli, *Helv. Chim. Acta*, 1933, 16, 169; *Chem. Abs.*, 1933, 27, 2154. See also R. D. Haworth, *J.C.S.*, 1932, 2717.



Much of the new light on this structure was given by studies in the diene synthesis. (See Chapter 40.) The reaction of methyl abietate and maleic anhydride at  $160^{\circ}\text{C}$ . yields an additive compound of the formula  $\text{C}_{26}\text{H}_{34}\text{O}_5$  which on hydrolysis passes over into the anhydride-carboxylic acid  $\text{C}_{24}\text{H}_{32}\text{O}_5$ . This same compound is obtained from American colophony by direct treatment with maleic anhydride. The fact that maleic anhydride does react indicates that a diene system exists in part.<sup>11</sup> There is only a partial reaction of ethyl abietate with maleic anhydride, showing that the natural acid is a mixture of isomerides.

All investigators do not agree with the above formula. There is still some disagreement on the position of the carboxyl group<sup>12</sup> though the principal controversy is on the position of the two double bonds. Vocke<sup>13</sup> placed them in the 7, 8 and 9, 14 positions whereas Arbuzov<sup>14</sup> suggested either the 7, 8 and 13, 14 or the 6, 7 and 5, 13 positions.<sup>15</sup>

Many methods have been devised for obtaining pure abietic acid from rosin.<sup>16</sup> (Crystals of abietic acid are shown in Figure 119.) The presence of resene exerts some influence on the reactivity of abietic acid, interfering with esterification and promoting oxidation.<sup>17</sup> One of the earliest ways of procuring pure abietic acid was to digest rosin with 70-90 per cent alcohol, precipitate with hydrochloric

<sup>11</sup> See B. Arbuzov, *Gen. Chem. (U. S. S. R.)*, 1932, 2, 806; *Chem. Abs.*, 1933, 27, 2688; *Brit. Chem. Abs. A*, 1933, 392.

<sup>12</sup> For instance, M. Farnica (*Bull. inst. pin.*, 1933, 151, 181; *Chem. Abs.*, 1934, 28, 160) places the carboxyl group in position 4.

<sup>13</sup> F. Vocke, *Ann.*, 1932, 497, 247; *Chem. Abs.*, 1932, 26, 5950.

<sup>14</sup> B. Arbuzov, *loc. cit.*

<sup>15</sup> For other work on the constitution of abietic acid see A. Tschirch and B. Studer, *Arch. Pharm.*, 1903, 241, 495; *J.C.S.*, 1904, 86 (1), 79. L. Ruzicka and J. Meyer, *Helv. Chim. Acta*, 1922, 5, 315; *Chem. Abs.*, 1922, 16, 2500. L. Ruzicka, H. Schinz and J. Meyer, *Helv. Chim. Acta*, 1923, 6, 1077; *J.C.S.*, 1924, 126 (1), 171. L. Ruzicka and M. Pfeiffer, *Helv. Chim. Acta*, 1925, 8, 632; *Chem. Abs.*, 1926, 20, 421. S. P. Serebrovski and M. M. Soloveva, *Zhur. Priklad. Khim.*, 1930, 3, 1199; *Chem. Abs.*, 1931, 25, 3349. L. Ruzicka, M. W. Goldberg, H. W. Huyser and C. F. Seidel, *Helv. Chim. Acta*, 1931, 14, 545; *Chem. Abs.*, 1931, 25, 3657. P. Levy and H. Tillmanns, *Ber.*, 1931, 64, 2441; *Chem. Abs.*, 1932, 26, 470. R. D. Haworth, B. M. Letsky and C. R. Mavin, *J.C.S.*, 1932, 1784. J. C. Bardhan and S. C. Sengupta, *J.C.S.*, 1932, 2798. L. Ruzicka and H. Waldmann, *Helv. Chim. Acta*, 1933, 16, 842; *Chem. Abs.*, 1933, 27, 4809. See also O. Aschan, *Ber.*, 1922, 55, 2944; *Chem. Abs.*, 1923, 17, 1228; *Chem.-Ztg.*, 1925, 49, 689; *Chem. Abs.*, 1925, 19, 3465. A. Madinavetia, *Anales soc. españ. fis. quim.*, 1922, 20, 183; *Chem. Abs.*, 1923, 17, 288.

<sup>16</sup> An approach to the synthesis of an acid of the abietic series has been made by M. T. Bogert and T. Hasselström (*Proc. Natl. Acad. Sci.*, 1932, 18, 417; *Chem. Abs.*, 1932, 26, 4326).

<sup>17</sup> C. C. Kesler, A. Lowy and W. F. Faragher, *J.A.C.S.*, 1927, 49, 2898.

acid, and recrystallize in methyl alcohol.<sup>22</sup> In the method of Steele<sup>23</sup> rosin is boiled under reflux for 2 hours in 98 per cent acetic acid. The mixture is then filtered and the filtrate allowed to crystallize.

In the opinion of Dupont and co-workers<sup>24</sup> abietic acid is not present as such in rosin, but is formed by isomerization at high temperatures<sup>25</sup> or under the influence of strong acids. Isomerization is obtained by passing a slow stream of hydrogen chloride through fused rosin at 150°C. for 15 minutes or by boiling an alcoholic rosin solution with concentrated hydrochloric acid. Abietic acid is purified by suspending rosin in alcohol and adding enough alkali to neutralize one-fourth of the acid.<sup>26</sup> An acid salt,  $C_{30}H_{48}O_8Na \cdot 3C_{30}H_{48}O_8$ , crystallizes out<sup>27</sup> which may be separated and further saponified to yield pure rosin soaps or may be decomposed by strong acids to regenerate pure abietic acid.<sup>28</sup>

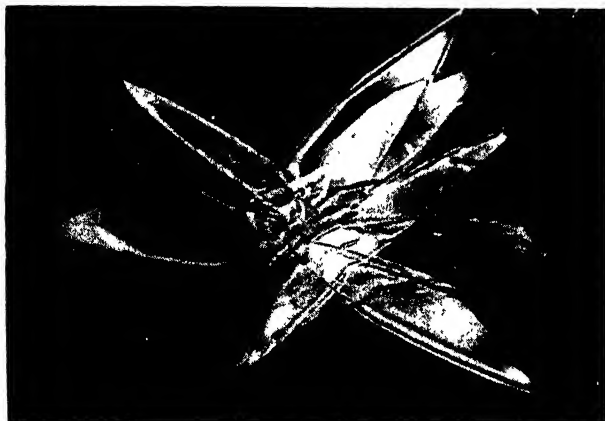


FIG. 119.

Typical Cluster of Abietic Acid Crystals. (O. A. Pickett and J. M. Schantz.)

Courtesy Industrial and Engineering Chemistry

Kressman<sup>29</sup> employed a distillation method for the separation of abietic acid and resene. The distillation is carried out at less than 10 mm. pressure in order to avoid decomposition. Under these conditions resene distills principally at 205-240°C. and abietic acid at 240-260°C. A somewhat similar method was used by Gammay.<sup>30</sup> He assumed that no resene is present in crude turpentine gum but that it is formed in the usual distillation method for obtaining rosin and spirit of turpentine. By distilling crude gum *in vacuo* below 110°C. with a small amount of saturated steam, Gammay obtained in 72 per cent yield a rosin with 0.8 per cent resene.

The vacuum-distillation (2 mm. press.) of wood rosin yields a fraction containing 93 per cent abietic acid which can be purified by dissolving in 80 per cent ethyl

<sup>22</sup> H. Mach, *Monatsh.*, 1893, 14, 186; *J.C.S.*, 1893, 64 (1), 582.

<sup>23</sup> L. L. Steele, *J.A.C.S.*, 1923, 44, 1833.

<sup>24</sup> G. Dupont and R. Usac, *Chimie et industrie*, 1925, (Sept. Special No.), 482; *Chem. Abs.*, 1926, 20, 612.

<sup>25</sup> See L. Pirjatinski and S. Nasakin, *Masloboino-Zhir. Delo*, 1930, 60-1, 56; *Chem. Abs.*, 1932, 26, 823.

<sup>26</sup> G. H. Dupont, U. S. P. 1,628,535, May 10, 1927; *Chem. Abs.*, 1927, 21, 2137. British P. 244,980, 1925; *Brit. Chem. Abs. B*, 1926, 202.

<sup>27</sup> See G. Dupont, L. Desalbres and A. Bernette, *Bull. soc. chim.*, 1926, 39, 488; *Brit. Chem. Abs. A*, 1926, 611.

<sup>28</sup> By using essentially this same method C. C. Kesler (U. S. P. 1,663,764, Mar. 27, 1928, and 1,894,374, Jan. 17, 1933, to Pine Institute of America, Inc.; *Chem. Abs.*, 1928, 22, 1698; 1933, 27, 2591) recovered resene for use in varnish. Similarly, benzene was used as the solvent and alcoholic potash as the saponifying agent by K. Schmidinger (U.S.P. 1,663,733, Mar. 27, 1928; *Chem. Abs.*, 1928, 22, 1695).

<sup>29</sup> F. W. Kressman, British P. 354,333, 1929; *Chem. Abs.*, 1932, 26, 3945. French P. 689,731, 1930; *Chem. Abs.*, 1931, 25, 1071. Canadian P. 810,774, 1931; *Chem. Abs.*, 1931, 25, 3185.

<sup>30</sup> H. Gammay, French P. 690,968, 1930; *Chem. Abs.*, 1931, 25, 1400.

alcohol and recrystallizing.<sup>27</sup> The mother-liquor is concentrated and its residues are fractionally distilled for further recovery of abietic acid.

Pure abietic acid can be prepared also by steam-distillation.<sup>28</sup> It is believed that highly superheated steam causes a physical dispersion of the aggregated molecules in rosin so that in steam-distillation very little decomposition occurs. Abietic acid is obtained in 86-96 per cent yield in distillation at 240-250°C.

Gnaedinger<sup>29</sup> obtained  $\alpha$ -abietic acid by heating French rosin with oxalic acid at 140-160°C. The resulting product is purified by crystallization in alcohol. Abietic anhydride (m.p. 149°C.) is obtained by boiling pure abietic acid with acetic acid anhydride.<sup>30</sup> Another method of obtaining abietic anhydride was used by Mossgraber.<sup>31</sup> Rosin is dissolved in ethyl alcohol containing 10 per cent of caustic soda. The solution is treated with acetyl chloride, and upon heating, ethyl acetate distills off leaving a residue of sodium chloride and abietic anhydride. The use of the latter in insulating-varnishes was suggested.

#### PURIFICATION OF ROSIN

Low-grade rosins are objectionable in the making of soaps because of the discoloration imparted by impurities. Consequently a number of methods have been devised for purifying rosin.<sup>32</sup> In one method, after the usual distillation of crude turpentine the distillation is continued under very high vacuum to produce a pure colophony.<sup>33</sup> For the purification of wood rosin it is distilled repeatedly at 270-330°C. under such sufficiently reduced pressure that very little decomposition occurs.<sup>34</sup> A continuous process for low-pressure distillation of wood rosin was devised by Schultze.<sup>35</sup> The material is heated to 180-255°C. and the resulting liquid is spread in a thin layer 3 to 4 mm. thick on a surface heated to about the same temperature as the liquid introduced. The desired pressure (as low as 1 mm.) is maintained over this surface, the vapors are collected and condensed and the non-volatile portion is removed from the surface continuously. An analogous method was used by Gubelmann and Lee.<sup>36</sup> It is stated that partial decolorization of low-grade rosin is effected by low-pressure distillation (10-20 mm.) at 250-290°C. in the presence of 0.3-1.0 per cent boric acid or borax.<sup>37</sup>

In a distillation method used by Hitch<sup>38</sup> the rosin is dissolved in turpentine or gasoline and the solution is sprayed into a zone heated to about 340°C. and kept under high vacuum so that vaporization is almost instantaneous. The purified rosin is collected by fractional condensation, it condensing at a lower temperature (about 210°C.) than the color-containing impurities (about 270°C.).

It was found by Hall<sup>39</sup> that the dark color of some rosins is caused by the oxidation or decomposition of constituents of acid and carbohydrate nature. Since these constituents are water-soluble in the original oleoresin it was suggested that lighter

<sup>27</sup> I. Gubelmann, C. O. Henke and H. R. Lee, U. S. P. 1,846,639, Feb. 23, 1932, to Newport Industries, Inc.; *Chem. Abs.*, 1932, 26, 2586.

<sup>28</sup> H. H. Wulicenus and H. Liang, *Z. angew. Chem.*, 1927, 40, 1500; *Brit. Chem. Abs. B*, 1928, 177.

<sup>29</sup> J. Gnaedinger, French P. 665,424 and 665,425, 1928; *Chem. Abs.*, 1930, 24, 984.

<sup>30</sup> E. Fonrobert, *Chem. Umschau Fette, Oele, Wachse, Harze*, 1929, 36, 373; *Chem. Abs.*, 1930, 24, 1386.

<sup>31</sup> E. Mossgraber, British P. 367,874, 1930; *Brit. Chem. Abs. B*, 1932, 475.

<sup>32</sup> Purification as applied here refers to the removal of objectionable constituents.

<sup>33</sup> C. Granel and J. Boulin, French P. 720,759, 1930; *Chem. Abs.*, 1932, 26, 4191.

<sup>34</sup> I. W. Humphrey, U. S. P. 1,832,804, Nov. 24, 1931, to Hercules Powder Co.; *Chem. Abs.*, 1932, 26, 1143. See also M. G. Donk, U. S. P. 1,219,413, Mar. 13, 1917; *Chem. Abs.*, 1917, 11, 1758.

<sup>35</sup> W. Schultze, U. S. P. 1,903,573, April 11, 1933; *Chem. Abs.*, 1933, 27, 3350.

<sup>36</sup> I. Gubelmann and H. R. Lee, U. S. P. 1,846,631, Feb. 23, 1932, to Newport Industries, Inc.; *Chem. Abs.*, 1932, 26, 2586.

<sup>37</sup> J. N. Borglin, U. S. P. 1,849,537, March 15, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1932, 26, 2579.

<sup>38</sup> A. R. Hitch, U. S. P. 1,904,464, Apr. 18, 1933, to Gillican-Chiple Co.; *Chem. Abs.*, 1933, 27, 3628.

<sup>39</sup> J. A. Hall, *Ind. Eng. Chem.*, 1932, 24, 1247.

rosins can be produced by washing the oleoresin with steam before distilling. Factors to control in the process include prevention of exposure of the gum to oxidation and use of apparatus free from iron.

Humphrey<sup>40</sup> treated impure rosin with a low-boiling hydrocarbon (boiling point less than 15°C. e.g., liquid butane) having a selective solvent action for the pure rosin. The solution is separated from the impurities and the rosin (75 per cent yield) is recovered by evaporation of the solvent. In similar methods methyl alcohol or a polyhydric alcohol is used.<sup>41</sup>

A different process consists in dissolving rosin in a solvent such as gasoline and treating with an organic ester (e.g., monacetin) which is immiscible with the rosin solution but dissolves out the coloring matter.<sup>42</sup> Other substances used as selective solvents include alcohols and glycols, phenols and such ethers as guaiacol or ethylene glycol monoethyl ether.<sup>43</sup>

A gasoline solution of rosin is freed of impurities by precipitation with an anhydrous metal chloride (e.g., zinc or stannic chloride).<sup>44</sup> Logan<sup>45</sup> employed essentially the same method using light-colored metal halides to precipitate the impurities from a 10 per cent solution of rosin in naphtha. To remove iron compounds rosin is treated in liquid phase with either oxalic or citric acid and the resulting product is extracted with petroleum naphtha.<sup>46</sup>

In a process of Palmer and Henke<sup>47</sup> rosin is dissolved in petroleum naphtha and resorcinol (90% aq.soln.) is added at 90-110°C. The mixture is stirred and allowed to settle so that the resorcinol layer containing the impurities can be separated. For further purification the rosin is treated with fuller's earth or charcoal.<sup>48</sup>

Resorcinol was used also by Borglin<sup>49</sup> as a solvent for rosin impurities. The rosin is dissolved in gasoline and the resorcinol is dissolved in an aliphatic alcohol (e.g., ethyl alcohol) with which the rosin solvent is immiscible. The two solutions are mixed together to dissolve the impurities and then are easily separated for the recovery of the pure rosin. In another of Borglin's methods the second solution consists of oxalic acid in 92 per cent ethyl alcohol.<sup>50</sup>

Kaiser and Hancock<sup>51</sup> used furfural as a selective solvent for rosin impurities. Low-grade wood rosin is dissolved in gasoline and then furfural is added. On refrigeration a layer settles out containing some rosin and a major portion of the furfural in which the impurities are contained. The remaining solution yields high-grade wood rosin in 70-75 per cent yield. A medium-grade rosin is recovered from the impure layer by gasoline extraction. In a modification of the process the furfural is replaced by either a phenol, a chlorohydrin, furfuryl alcohol,

<sup>40</sup> I. W. Humphrey, U. S. P. 1,806,973, May 26, 1931, to Hercules Powder Co.; *Chem. Abs.*, 1931, 25, 4189.

<sup>41</sup> I. W. Humphrey, U. S. P. 1,852,245, Apr. 5, 1932, and 1,897,379, Feb. 14, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1932, 26, 3109; 1933, 27, 2881.

<sup>42</sup> I. W. Humphrey, U. S. P. 1,890,986, Dec. 6, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 1774.

<sup>43</sup> I. W. Humphrey, U. S. P. 1,800,834, Apr. 14, 1931, and 1,905,173, Apr. 25, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1931, 25, 3503; 1933, 27, 3628.

<sup>44</sup> I. W. Humphrey, U. S. P. 1,887,097, Nov. 8, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 1503. See also J. N. Borglin, U. S. P. 1,804,975, Jan. 24, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 2592.

<sup>45</sup> W. B. Logan, U. S. P. 1,782,267, Nov. 18, 1930, to Newport Co.; *Chem. Abs.*, 1931, 25, 424.

<sup>46</sup> A. F. Oliver and R. C. Palmer, U. S. P. 1,881,893, Oct. 11, 1932, to Newport Industries, Inc.; *Chem. Abs.*, 1933, 27, 616.

<sup>47</sup> R. C. Palmer and C. O. Henke, U. S. P. 1,791,633, Feb. 10, 1931, to Newport Co.; *Chem. Abs.*, 1931, 25, 1012. British P. 294,526, 1928; *Brit. Chem. Abs.* B, 1930, 157. See also R. C. Palmer, J. L. Burda and A. F. Oliver, U. S. P. 1,787,588, May 6, 1930; *Chem. Abs.*, 1930, 24, 3387, and I. Gubelmann and C. O. Henke, U. S. P. 1,810,170, June 16, 1931; *Chem. Abs.*, 1931, 25, 4725.

<sup>48</sup> R. C. Palmer, U. S. P. 1,810,222, June 16, 1931, to Newport Co.; *Chem. Abs.*, 1931, 25, 4725.

<sup>49</sup> J. N. Borglin, U. S. P. 1,901,626, Mar. 14, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 2350.

<sup>50</sup> J. N. Borglin, U. S. P. 1,959,544, May 22, 1934, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 4616.

<sup>51</sup> H. E. Kaiser and R. S. Hancock, British P. 253,082, 1926, to Hercules Powder Co.; *Brit. Chem. Abs.* B, 1926, 988. See French P. 621,411, 1926; *Chem. Zentr.*, 1927, 2, 645.

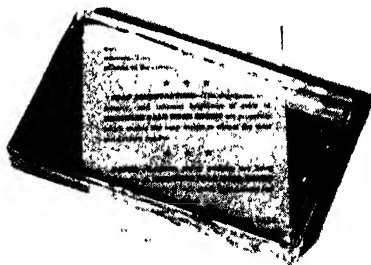


sulphur dioxide or aniline.<sup>53</sup> Hancock<sup>54</sup> treated rosin (dissolved in gasoline) with furfural or phenol to remove impurities and then subjected the refined rosin to vacuum-distillation for further purification.<sup>54</sup>

Humphrey<sup>55</sup> removed coloring matter by condensing rosin with an aldehyde and ammonia or with hexamethylenetetramine and distilling the product under reduced pressure. A similar procedure was described by Zilberman and others.<sup>56</sup> A condensation product is formed by heating 100 parts of rosin for 24 hours with 25 parts of 40 per cent formaldehyde solution and 0.1 part of hydrochloric acid.

Fig. 120.

Illustrating the Clarity of Wood Rosin  
(O. A. Pickett and J. M. Schantz.)



Courtesy Industrial and Engineering Chemistry

This product is distilled at 300°C. under reduced pressure to recover pure colophony.

The process used by Hey<sup>57</sup> consists in dissolving rosin in an organic solvent and submitting it to the action of zinc and hydrochloric acid. The rosin solution is placed in a container having one wall made of zinc provided with small perforations, and this container is immersed in an aqueous hydrochloric acid solution containing zinc. The rosin solution passes through the perforations into the acid solution where it is thoroughly agitated and then allowed to rise to the surface.

Purification of rosin by means of hydrogenation was used by Henke.<sup>58</sup> A catalyst such as nickel is used in the process, and after its removal the hydrogenated product is distilled (250-300°C. under 10 mm. or less pressure) and an intermediate fraction is collected (70-75 per cent yield). An absorption of 90 per cent of the theoretical amount of hydrogen is possible if rosin is dissolved in amyl alcohol and a small amount of concentrated hydrochloric acid and treated at 145°C. with hydrogen under 7 atmospheres pressure.<sup>59</sup> Palladium is used as the catalyst in this case.

<sup>53</sup> British P. 275,862, 1927, addn. to 253,082, to Hercules Powder Co.; *Brit. Chem. Abs.* B, 1927, 822. French P. 632,838, 1927; *Chem. Abs.*, 1928, 22, 3543.

<sup>54</sup> R. S. Hancock, U. S. P. 1,908,754, May 16, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 3836.

<sup>55</sup> See also A. G. Jevdokimov, *J. Appl. Chem. (U. S. S. R)*, 1933, 6, 933; *Brit. Chem. Abs.* B, 1934, 71.

<sup>56</sup> I. W. Humphrey, U. S. P. 1,887,157, Nov. 8, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 1503.

<sup>57</sup> G. Zilberman, A. Bolotin and P. Romanova, *Lakokrasochnaya Ind.*, 1933 (3), 21; *Chem. Abs.*, 1933, 27, 5202.

<sup>58</sup> E. Hey, U. S. P. 1,912,037, May 30, 1933; *Chem. Abs.*, 1933, 27, 4072.

<sup>59</sup> C. O. Henke, U. S. P. 1,899,961, March 7, 1933, to Newport Industries, Inc.; *Chem. Abs.*, 1933, 27, 3095. See also Carleton Ellis, U. S. P. 1,249,050, Dec. 4, 1917; *Chem. Abs.*, 1918, 12, 432. B. T. Brooks, U. S. P. 1,167,264, Jan. 4, 1916; *Chem. Abs.*, 1916, 10, 698.

<sup>60</sup> B. Tyutyunnikov and N. Perstnev, *Allgem. Öl-u. Fett.-Ztg.*, 1931, 28, 319; *Chem. Abs.*, 1932, 26, 3395. See British P. 356,742, 1929, to Chem. Fabrik Dr. K. Albert G.m.b.H.; *Chem. Abs.*, 1933, 26, 4488.

It was found by Palmer, Burda and Oliver<sup>60</sup> that the suggested use of fuller's earth in decolorizing rosin<sup>61</sup> did not apply very well in the case of wood rosin. Excessive amounts of earth had to be used because of the presence of terpenes which by partial polymerization cause gummy precipitates on the filter. In addition, the terpenes which do not polymerize act as solvents for the rosin impurities, preventing their adhesion to the fuller's earth. To remove the terpenes the rosin is distilled with dry steam at elevated temperatures. The residue is dissolved in a petroleum distillate (boiling 100-160°C.) and cooled to about 20°C. to precipitate petroleum-insoluble matter and is then filtered through fuller's earth. In one method of filtering a series of beds is used and as the first bed becomes saturated with impurities it is cut out of the group and is replaced by a fresh filter placed last in the series, each of the other filters then being advanced one position in the group.<sup>62</sup>

In a process used by Brooks<sup>63</sup> for purifying natural resins the crude material is mixed with a chlorohydrin of a gaseous olefin (e.g., ethylene- or propylenechlorohydrin) to form a thin viscous mixture. A temperature of 60-70°C. is normally employed. The proportion of resin to chlorohydrin is usually 1 to 5. Impurities are removed by filtration and the resin is recovered by vacuum-distillation of the chlorohydrin. Tournel<sup>64</sup> converted rosin into potassium resinate in order to separate impurities. The rosin (1 part) is powdered and suspended in 3 parts of water which is then heated to boiling and treated with 1 part of caustic potash solution (sp. gr. 1.33). When a pasty consistency has been obtained 8 parts of water are added and the boiling is continued for 15 minutes. The resinate is coagulated with an electrolyte and the supernatant liquid containing the impurities is siphoned off. The resinate is again suspended in water and is treated with sodium carbonate and a small amount of sodium peroxide (1 per cent). The boiling is continued and the resinate is recoagulated with sodium chloride and hydrochloric acid.

In order to obtain a rosin which would not tend to crystallize, Palmer<sup>65</sup> treated wood rosin in naphtha solution with sufficient caustic alkali to neutralize from 3 to 6 per cent of the abietic acid in the rosin. A reduction in crystallizing tendency and an improvement in color results when rosin is subjected to a heat treatment (280-350°C.) for half an hour in an inert atmosphere such as carbon dioxide.<sup>66</sup> By heating wood rosin at 260-325°C. Logan<sup>67</sup> effected a reduction in the crystallization tendency and at the same time increased the optical rotation.<sup>68</sup> It appeared that the alteration in optical rotation is directly proportional to the lowering of the crystallization tendency. By heating wood rosin at 300°C. for two hours the optical rotation changes from +4 to about +25. At the same time the discoloring impurities are made soluble in rosin solvents. It was later found that this same treatment removes what are designated "potential color bodies" from rosin which has already been bleached.<sup>69</sup> Although bleached rosin appears to be free of coloring matter it tends to develop a yellowish color when converted into an alkali soap

<sup>60</sup> R. C. Palmer, J. L. Burda and A. F. Oliver, U. S. P. 1,807,599, June 2, 1931; *Chem. Abs.*, 1931, 25, 4422.

<sup>61</sup> See A. R. Autrey, U. S. P. 1,559,399, Oct. 27, 1925; *Chem. Abs.*, 1926, 20, 283.

<sup>62</sup> R. C. Palmer, J. L. Burda and A. F. Oliver, U. S. P. 1,905,493, Apr. 25, 1933, to Newport Industries, Inc.; *Chem. Abs.*, 1933, 27, 3623.

<sup>63</sup> B. T. Brooks, U. S. P. 1,340,873, May 25, 1920, to the Commercial Research Corp.; *Chem. Abs.*, 1920, 14, 2270.

<sup>64</sup> M. Tournel, French P. 693,292, 1929; *Chem. Abs.*, 1931, 25, 1692.

<sup>65</sup> R. C. Palmer, U. S. P. 1,787,281, Dec. 30, 1930, to Newport Co.; *Chem. Abs.*, 1931, 25, 835.

<sup>66</sup> D. C. Butts, U. S. P. 1,791,658, Feb. 10, 1931, to Hercules Powder Co.; *Chem. Abs.*, 1931, 25, 3012.

<sup>67</sup> W. B. Logan, U. S. P. 1,642,276, Sept. 20, 1927, to Acme Products Co., Inc.; *Chem. Abs.*, 1927, 21, 3756.

<sup>68</sup> A study of optical rotation and crystal structure of rosin acids is discussed by E. A. Georgi, *J. Chem. Education*, 1933, 10, 415; *Chem. Abs.*, 1933, 27, 4106.

<sup>69</sup> W. B. Logan, U. S. P. 1,807,489, May 26, 1931, to Newport Co.; *Chem. Abs.*, 1931, 25, 4189.

and precipitated with aluminum salts. This is of course objectionable if the material is used in sizing paper.

It was stated by Humphrey<sup>70</sup> that a composition which will not crystallize can be produced by mixing rosin with about 15 per cent or less of a rosin-distillation residue. This mixture can be used in core oils, varnishes and printing inks.

### LIMING OF ROSIN

Untreated rosin is unsatisfactory for use in varnishes directly for many reasons. It is too soft and is neither waterproof nor durable. If a solution of rosin in benzene is brushed out on a surface the resulting film when dry will attain a high gloss, but in a short time it will become dull. In warm weather the film will become sticky, possessing what is known as the printing effect. In damp weather there will appear on the film a bluish opalescence or "bloom," evidently caused by surface-absorption of moisture by the resin acid. All these qualities are to be found in varnishes containing rosin as such in considerable quantities. Rosin is used to a small extent to assist the solution of natural gums and fossil resins, but the temptation to use larger proportions is great because of its relative cheapness.

Another objection to the acid nature of rosin is its influence on the "livering" of varnishes, a peculiar thickening which occurs when basic pigments are ground with varnishes. Thickening is due principally to colloid reactions causing molecular aggregation and gel formation.<sup>71</sup> The rate of living increases with the acidity of the varnish.<sup>72</sup>

It was discovered long ago that rosin becomes harder and less sticky by partial neutralization with lime.<sup>73a</sup> Rosin so treated is known in industry as "lime-hardened rosin," "limed rosin" or simply "hardened rosin." A hardened rosin varnish will hold its gloss longer than one from ordinary rosin.

The customary method of liming rosin is by fusion. Complete neutralization cannot be effected in this manner, nor is it desirable. A completely or nearly completely neutral lime soap is only partially soluble in the common varnish oils and solvents. In the treatment of rosin with lime a purely neutral resinates is not formed, but rather a mixture of neutral and basic resinates, so that the acidity does not decrease in direct proportion to the amount of lime used. The ratio of basic to neutral resinates appears to increase with the amount of lime, and at the same time there is formed in the fused mass a suspensoid of hydrated lime which decreases the fusibility of the batch. Under these conditions the temperature

<sup>70</sup> I. W. Humphrey, U. S. P. 1,931,226, Oct. 17, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 352.

<sup>71</sup> C. Coffignier, *Bull. soc. chim.*, 1923, 33, 1558; 1924, 35, 898; *Chem. Abs.*, 1924, 18, 909; 1925, 19, 738; *Rev. gen. colloid.*, 1923, 1, 18; 1924, 2, 37; *Chem. Abs.*, 1924, 18, 1208, 2968. See also Carleton Ellis and L. Rabinovitch, *Ind. Eng. Chem.*, 1916, 8, 406. S. V. Yakubovitch and S. V. Kirsanova, *Kolloid-Z.*, 1933, 65, 333; *Chem. Abs.*, 1934, 28, 2201. F. Schmid, *Farbe u. Lack*, 1933, 172; *Chem. Abs.*, 1933, 27, 3349. Chicago Club report, *Amer. Paint and Varnish Mfrs. Assoc. Circ.*, 1933, 445, 459; 1934, 471, 289; *Chem. Abs.*, 1934, 28, 347; 1935, 29, 360. M. H. Fischer and W. J. Suer, *Kolloid-Z.*, 1932, 60, 71; *Chem. Abs.*, 1932, 26, 5219. H. Wagner, *ibid.*, 307; *Chem. Abs.*, 1932, 26, 6161. It has been stated, however, that thickened paints and varnishes can be restored by the addition of 0.5-10 per cent of free fatty acids. See T. F. Bradley, U. S. P. 1,478,017, Dec. 18, 1923, *J.S.C.I.*, 1924, 43, 224B.

<sup>72</sup> Although monobasic acids frequently increase the rate of living of varnishes it has been reported that tribasic acids, e.g., boric or phosphoric reduce living in some cases. See Schulmann, *Farbe u. Lack*, 1934, 307; *Brit. Chem. Abs.*, B, 1934, 725.

<sup>73a</sup> The use of lime for hardening rosin was advocated in 1884 by A. K. Kissel (U. S. P. 303,436, Aug. 12, 1884, to C. Zimmer. Reissue 10,714, Apr. 20, 1886. U. S. P. 414,366, Nov. 25, 1890. British P. 8036, 1884; German P. 30,000, 1884; French P. 162,098, 1884). Other bases were suggested also by Kissel, for instance, baryta or magnesia. J. B. Melvin (U. S. P. 370,640, Sept. 27, 1887; British P. 5270, 1886; *J.S.C.I.*, 1886, 3, 432) recommended zinc oxide and other metallic oxides. Carleton Ellis and H. M. Weber (U. S. P. 1,381,863, June 14, 1921; *Chem. Abs.*, 1921, 15, 3586) used calcium cyanamide. The use of 25-30 per cent of calcium acetate was suggested by M. Bottler (*Kunstst.*, 1913, 3, 84; *Chem. Abs.*, 1913, 7, 2314).

needed to liquefy the mass is so high that decomposition of the resinates occurs. For these reasons complete neutralization of rosin cannot be carried out by the fusion method. A pale, hardened rosin will not have much less than 30 per cent free rosin acid.<sup>73</sup>

For the liming operation a good grade of hydrated lime technically free from iron and containing less than 1 per cent of magnesium oxide should be chosen. Iron is objectionable because of the dark colors it imparts, and magnesium decreases the solubility of the product. Magnesium resinates have a greater viscosity than those of calcium resinate so that the presence of the former causes thickening of varnishes. Hydrated lime is preferred to quicklime because of its more flocculent condition, permitting it to react more readily with the rosin.<sup>74</sup> Also, in the reaction of hydrated lime with rosin, steam is evolved which serves to keep the lime in suspension, whereas quicklime will tend to settle to the bottom.<sup>75</sup>

A tentative specification made by Gardner<sup>76</sup> for hydrated lime to be used in varnish is: color, white; fineness, not more than 10 per cent over 250-mesh; reactivity, satisfactory in gloss-oil and tung-oil tests; calcium oxide, not less than 70 per cent (equivalent to 92.5 per cent calcium hydroxide); magnesium oxide, not more than 3 per cent; insoluble matter and oxides of iron and aluminum, not more than 2 per cent; carbon dioxide, not more than 2 per cent.

In ordinary practice the maximum amount of lime used is 6-8 per cent of the weight of rosin, the acid number of the rosin being reduced from 165 to 70 with 6 per cent of lime.<sup>77</sup> With this amount a transparent product should be obtained, but with higher percentages a cloudy effect is produced. Also, as was stated previously an overlimed rosin is not completely soluble in varnish oils and solvents. Therefore ordinarily 5-6 per cent of lime is used. The customary procedure is to heat the rosin to 300°C. to prevent crystallization, cool to 200°C. and stir in the lime gradually. Although ordinarily the lime is added dry it is said that somewhat better results are obtained by mixing it with a little linseed oil and water and adding 0.1 per cent calcium or lead acetate as a catalyst.<sup>78</sup> The temperature is then raised to 260°C. and the mixture is stirred to prevent settling of the lime. After all the lime has been taken up and the water has been driven off the rosin is poured into cooling pans. In order to get the best control of color and acidity large batches are cooked in closed kettles under careful supervision.

In the hardening of rosin other basic oxides are sometimes used in place of or in addition to lime.<sup>79</sup> For instance a grinding-varnish rosin is made by hardening rosin with 2 per cent of magnesium oxide and 5 per cent zinc oxide. The use of 4 per cent of slaked lime and 2-3 per cent of zinc oxide gives a rosin for rubbing-varnishes.<sup>80</sup> The method employed is to add zinc oxide at 220-240°C., continue

<sup>73</sup> A. Murray, *Chem. Met. Eng.*, 1921, 25, 473.

<sup>74</sup> The use of hydrated lime and of carbonate of lime and calcium sulphide in place of quicklime for hardening rosin was recommended by S. Banner (British P. 11,805, 1887; *J. S. C. I.*, 1888, 7, 573). The amount of hydrated lime used was 3-15 per cent. In some cases 3-7 per cent sulphur was used, the amount of lime then being reduced. See also C. Cofignier, *Chimie et industrie*, 1921, 5, 497; *Chem. Abs.*, 1921, 15, 2555.

<sup>75</sup> Manufacturers formerly favored the use of oyster-shell lime because although its calcium oxide content is comparatively low it is technically free from magnesium and iron salts and its composition is reasonably constant. The use of coral lime was recommended by W. H. Scheel (U. S. P. 1,428,120, Sept. 5, 1922, *Chem. Abs.*, 1922, 16, 3766).

<sup>76</sup> H. A. Gardner, *Paint Mfrs. Assoc. Circ.*, 1921, 113; *Chem. Abs.*, 1921, 15, 765.

<sup>77</sup> See J. McE. Sanderson, *Ind. Eng. Chem.*, 1934, 26, 711.

<sup>78</sup> See J. M. Schantz, *Paint. Oil, Chem. Rev.*, 1931, 92 (17), 9; *Chem. Abs.*, 1932, 26, 609. An organic carboxylic acid (particularly acetic), a halogen or a halogen acid or salt has been suggested as catalyst by E. V. Romaine, H. J. Weiland, P. O. Bowers and R. C. Palmer (U. S. P. 1,884,407, Oct. 25, 1932, to Newport Industries, Inc.; *Chem. Abs.*, 1933, 27, 1163).

<sup>79</sup> See O. Prager, *Seifen. Ztg.*, 1915, 42, 686, 705; *Chem. Abs.*, 1915, 9, 3369. In using metallic oxides pale-colored products are obtained if the oxides are in a finely divided state. See Krumbhaar, *J. Oil. Col. Chem. Assoc.*, 1934, 17, 413; *Brit. Chem. Abs. B.*, 1935, 160.

<sup>80</sup> F. Pirschel (U. S. P. 521,270, June 12, 1894) stated that by using rosin oil as a flux as much as 16 per cent of manganese dioxide, 10 per cent of barium oxide or 40 per cent of lead oxide could be absorbed by rosin.

heating until the mixture is clear, then add slaked lime and raise the temperature to 275°C. to complete the reaction.<sup>81</sup>

Natural resins other than rosin have been hardened with lime although such treatment renders them partially insoluble in turpentine or linseed oil and lowers their resistance to the action of water and the atmosphere.<sup>82</sup> Resins treated in this way include dammar and various copals such as Manila, kauri, Congo, Zanzibar and Hymenaea (S. American).

Similarly, the melting point of crude montan wax is raised by heating the wax with about 1 per cent of a metal hydroxide, basic oxide or carbonate in water at temperatures between 100°C and the melting point of the wax.<sup>83</sup> The treatment may be effected also by dissolving the wax in an organic solvent in which case the reaction is carried out at temperatures up to 200°C.

**Gloss Oil.** If lime-hardened rosin is dissolved in petroleum naphtha a very cheap variety of varnish is obtained. In industry this solution is known as "gloss oil," since it imparts a gloss to paints and varnishes in which it is used. Gloss oil is used to some extent in flat-white enamels and in cheap lacquers, tool varnishes, shingle stains and the like. Because of the free acid in gloss oil there is risk of yellowing<sup>84</sup> when it is used in flat-white paints, and when used in the priming coat for plaster or cement walls it ultimately causes crumbling.

Gloss oil may be prepared directly by melting rosin at about 150°C., thinning it with about an equal weight of mineral spirits and then adding the required amount of lime. The heating is continued at 110°C. until the lime has reacted, then the temperature is raised to 150°C. to remove water. Gloss oils prepared in this way using 10 per cent or less lime were still clear after 2 years aging.<sup>85</sup> In cases in which 12 per cent of lime had been used crystallization occurred.

A gloss oil, pale in color, was prepared by Davidson<sup>86</sup> by grinding the ingredients together in a pebble mill. It is stated that more lime can be introduced into rosin by this method than is used in the kettle method. If a varnish or enamel is to be made the pigment is ground with the rosin, lime and naphtha, and the other ingredients are added later.

Rosin and lime-hardened rosin are used extensively with tung oil (China wood oil) for the manufacture of varnishes. The characteristics of tung-rosin varnishes are pale color, rapidity of drying, high gloss, durability and waterproof qualities. A dried coating of gloss oil will promptly turn white on contact with water, and the same is true of a rosin-linseed oil varnish, although to a lesser degree.<sup>87</sup> A tung oil-rosin varnish, however, is highly resistant to water. Moreover, rosin acts as a good solvent for over-heated or gelatinized tung oil, and it has a retardant action on the polymerization of tung oil.<sup>88</sup> The use of lined rosin in place of raw rosin makes a harder and more quickly drying varnish but at the same time imparts brittleness.

Although some varnishes of this type consist simply of tung oil, rosin and thinners, others contain in addition linseed oil<sup>89</sup> or other oils and resins.<sup>90</sup> Con-

<sup>81</sup> H. Hadert, *Farben-Chem.*, 1934, 5, 409; *Brit. Chem. Abs.* B, 1935, 33.

<sup>82</sup> M. Bottler, *Chem. Rev. Fett-Harz-Ind.*, 1910, 17, 292; *Chem. Abs.*, 1911, 5, 1198.

<sup>83</sup> German P. 581,891, 1933, and its additions 583,333 and 583,484, 1933, to A. Riebeck'sche Montanwerke A.-G.; *Chem. Abs.*, 1934, 28, 1170.

<sup>84</sup> The yellowing of white enamels was attributed by H. Munzert (*Farben-Ztg.*, 1928, 33, 2849; *Brit. Chem. Abs.* B, 1928, 719) to the oxidation of resin acids.

<sup>85</sup> S. A. Levy, *Am. Paint, Varnish Mfrs. Assoc., Circ.*, 1931, 386, 208; *Chem. Abs.*, 1931, 25, 4417.

<sup>86</sup> D. Davidson, *Paint, Oil, Chem. Rev.*, 1928, 86 (5), 11; *Chem. Abs.*, 1928, 22, 3541.

<sup>87</sup> See F. C. Schmutz, F. C. Palmer and W. W. Kittleberger, *Ind. Eng. Chem.*, 1930, 22, 856.

<sup>88</sup> See R. Schwarz, *Farbe u. Lack*, 1931, 123; *Brit. Chem. Abs.* B, 1931, 895. H. Hadert, *ibid.*, 1928, 558; *Chem. Abs.*, 1929, 23, 721.

<sup>89</sup> A report of the results of 21 various procedures of making up varnishes of hardened rosin, tung oil, linseed oil and petroleum thinner was made by E. C. Hannes, *Am. Paint, Varn. Mfrs. Assoc. Circ.*, 1931, 404, 619; *Chem. Abs.*, 1932, 26, 1140.

<sup>90</sup> See, for example, L. Auer, *British P.* 341,431, 1929, *Brit. Chem. Abs.* B, 1931, 451, and J. B. Diets

siderable study has been made on the cause of blooming in varnish films.<sup>91</sup> Krumbhaar<sup>92</sup> stated that a linseed oil-rosin varnish must contain at least 3 parts of oil to 2 of rosin to be free from bloom. According to Harrison and Fonrobert<sup>93</sup> factors which may produce blooming are excessive amounts of driers and free acids, certain thinners, improperly refined or cooked oils and improperly run resins. It has been pointed out that the presence of too much lime-hardened rosin will also cause blooming.<sup>94</sup>

#### VARIOUS METHODS OF HARDENING ROSIN

In addition to liming, other methods of hardening rosin have been devised.<sup>95</sup> Many of these include oxidation by various means.<sup>96</sup> One of the earliest consisted merely in passing a current of air or oxygen through molten rosin.<sup>97</sup> Another method is to use this same treatment with the addition of 1 to 5 per cent of a phenol or phenol ester which is said to impart toughness. A variation of this method consists in heating rosin with a ferric salt and hypochlorites.<sup>98</sup>

Schaal<sup>99</sup> passed a current of heated air or oxygen over powdered rosin, the temperature being kept below the melting point of the rosin.<sup>100</sup> The oxidized product is not soluble in oil of turpentine and fatty oils, and thus resembles fossil resins in that it must be heated above its melting point to render it soluble. In a modification of the Schaal process the powdered rosin (100 parts) is mixed with cobalt acetate (0.3 part) and anhydrous sodium sulphate (40 parts) and treated as described above.<sup>101</sup> The cobalt acetate can be replaced by either manganese resinate or manganese borate and a mixture of equal parts of sodium chloride and sodium sulphate can be used instead of the latter alone. After the hardening process the rosin is washed well with warm water and dried by slight melting or fusing.

It was observed by Miles<sup>102</sup> that the mere exposure of powdered rosin to air produces only slow oxidation probably caused by a film of inert gas on the rosin surface preventing the access of fresh oxygen. This difficulty is removed by moistening the rosin with water. The powdered rosin can be treated with a solution of hydrogen peroxide or it can be agitated with water and treated with ozone. The oxidation is promoted by mixing with the rosin such substances as calcium hypochlorite, formaldehyde, dilute sulphuric or sulphurous acid, milk of lime, soda ash and turpentine.<sup>103</sup> It was stated that rosin oxidized in this manner yields when

and E. F. Oeffinger, U. S. P. 1,942,413, Jan. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1879.

<sup>91</sup> See N. K. Adam and R. S. Morrell, *J.S.C.I.*, 1934, 53, 255T. N. K. Adam, R. S. Morrell and H. Samuels, *ibid.*, 280T. R. Priester, *Verfkroniek*, 1932, 5, 17; *Chem. Abs.*, 1932, 26, 2332.

<sup>92</sup> W. Krumbhaar, *Am. Paint, Varn. Mfrs. Assoc. Ctr.*, 1930, 370, 520; *Chem. Abs.*, 1931, 25, 221.

<sup>93</sup> A. W. C. Harrison and E. Fonrobert, *Farben-Ztg.*, 1931, 36, 1467, 1512, 1554, 1601, 1645; *Chem. Abs.*, 1931, 25, 5046. See also H. Nolte, *Farbe u. Lack*, 1932, 413, 425, 439; *Chem. Abs.*, 1932, 26, 5775.

<sup>94</sup> See *Farbe u. Lack*, 1928, 349; *Chem. Abs.*, 1928, 22, 4842. H. Wolff, *Farben-Ztg.*, 1930, 36, 505; *Chem. Abs.*, 1931, 25, 1106. See also S. Yakubovick and K. Terekhov, *Malyarnoe Delo*, 1932 (7), 24; *Chem. Abs.*, 1934, 28, 800.

<sup>95</sup> R. C. Palmer and A. F. Oliver (U. S. P. 1,881,907, Oct. 11, 1932, to Newport Industries, Inc.; *Chem. Abs.*, 1933, 27, 616) raised the melting point of rosin by heating it for 1-8 hours at 260-300°C. ("solrosing") and then distilling the highly volatile constituents.

<sup>96</sup> The oxidation of rosin causes a darkening in color. See A. R. Hitch, *Ind. Eng. Chem.*, 1931, 23, 1276.

<sup>97</sup> British P. 7625, 1901, to Elekt. A.-G. vorm. Schuckert & Co.; *J.S.C.I.*, 1901, 20, 729. See also Austrian P. 130,464, 1932, to Landwirts. Genossenschaft zur Verwertung der Harzprodukte; *Chem. Abs.*, 1933, 27, 1085.

<sup>98</sup> German P. 346,306, 1920, to Plauson's Forschungsinst. G.m.b.H.; *J.S.C.I.*, 1922, 41, 261A.

<sup>99</sup> E. Schaal and M. Schaal, U. S. P. 698,741, Apr. 29, 1902; *J.S.C.I.*, 1902, 21, 782. British P. 4615, 1900; *J.S.C.I.*, 1901, 20, 263.

<sup>100</sup> It is stated that a similar treatment of copals renders them useful in oil-, spirit- or nitrocellulose varnishes. (A. Stiel, British P. 353,389, 1929, and German P. 548,304, 1929; *Chem. Abs.*, 1932, 26, 3686.)

<sup>101</sup> E. Schaal, U. S. P. 1,533,014, May 4, 1926; *Chem. Abs.*, 1926, 20, 2082. British P. 243,556, 1925; *Chem. Abs.*, 1926, 20, 3826.

<sup>102</sup> G. W. Miles, U. S. P. 1,410,211, Mar. 21, 1922, to Ross Chemical Co.; *Chem. Abs.*, 1922, 16, 1875.

<sup>103</sup> G. W. Miles, U. S. P. 1,401,348, Dec. 27, 1921; *Chem. Abs.*, 1922, 16, 1013.

neutralized with ammonia a soap which is quite soluble in water. This rosin-ammoniate is used for coating various materials (e.g., paper). Whipple<sup>104</sup> improved the electrical insulating properties of rosin by passing moist air through molten rosin at 135°C. and then treating the melt at 140°C. with dry air. Other methods<sup>105</sup> of oxidizing rosin include passing air or oxygen or ozonized air into solutions of the material in non-aromatic hydrocarbons<sup>106</sup> or such solvents as glacial acetic acid.<sup>107</sup> Pungs<sup>108</sup> oxidized mixtures of waxes and rosin by passing heated air (160-170°C.) through the mixture in a retort charged with inert heat-conducting material.

In connection with the oxidation of rosin the observations of Korotkov and Rufinski prove interesting. Rufinski<sup>109</sup> found that the melting point of rosin is raised at least 12 degrees by blowing air through the molten rosin at 130-150°C for 10 hours and that the addition of 1 per cent calcium oxide and blowing at 200-212°C. for 6 hours raised the melting point of rosin to 107°C. The investigations of Korotkov<sup>110</sup> show that the ability of rosin to absorb oxygen spontaneously<sup>111</sup> depends on the temperature of its preparation from crude turpentine gum. The most stable rosins are prepared at 200-270°C. The oxidation of rosin decreases the iodine number 74-78 per cent and the acid number 12-18 per cent. In the opinion of Scheiber<sup>112</sup> the variations in the solubility of rosin in benzine are caused by the presence of products of auto-oxidation.<sup>113</sup>

One of the uses suggested for oxidized rosin is as a solvent for nitrocellulose in lacquers.<sup>114</sup> A similar application is in a shellac substitute composed of oxidized rosin, cellulose esters and camphor or camphor substitutes.<sup>115</sup> Oxidized rosin has been used as an anti-coagulant in linoleum manufacture.<sup>116</sup>

It may be of interest to note here certain products obtained by the oxidation of substances similar to rosin. Among these are a thermoplastic material procured by oxidizing the semi-fluid resin occurring in crude gutta-percha and balat.<sup>117</sup> and a resinous mass produced in the oxidation of turpentine oils<sup>118</sup> and pine-tar oils.<sup>119</sup>

<sup>104</sup> D. Whipple, U. S. P. 1,083,168, 1,083,169 and 1,083,170, Dec. 30, 1913, to Standard Chemical Co.; *Chem. Abs.*, 1914, 8, 830, 831.

<sup>105</sup> The oxidation of rosin with nitric acid is discussed in Chapter 35

<sup>106</sup> A. S. Ramage, U. S. P. 1,752,693, Apr. 1, 1930; *Chem. Abs.*, 1930, 24, 2623

<sup>107</sup> German P. 434,419, 1922, to A. Riebeck'sche Montanwerke, A.-G.; *Brit. Chem. Abs.* B, 1927, 305.

<sup>108</sup> W. Pungs, U. S. P. 1,780,632, Nov. 4, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 226. British P. 258,099, 1925; *Brit. Chem. Abs.* B, 1926, 987. German P. 498,598, 1930, addn to 405,850, 1921; *Chem. Zentr.*, 1931, 1, 869; *J.S.C.I.*, 1925, 44, 179B

<sup>109</sup> P. Rufinski, *Masloboino Zhir Delo*, 1931 (1), 31, (10) 17; *Chem. Abs.*, 1932, 26, 4485.

<sup>110</sup> K. Korotkov, *J. Chem. Ind (Moscow)*, 1930, 7, 1165; *Chem. Abs.*, 1931, 25, 4137.

<sup>111</sup> The oxidation of rosin imparts photoactive properties. See G. Norkin and B. Shadin, *Chem. Umshau Fette, Öle, Wachse, Harze*, 1930, 37, 340; *Chem. Abs.*, 1931, 25, 1107.

<sup>112</sup> J. Scheiber, *Farbe u. Lack*, 1932, 644; *Chem. Abs.*, 1933, 27, 1527.

<sup>113</sup> Some information on the oxidation of rosin can be obtained from reports on the oxidation of abietic acid. See H. Mach, *Monatsh.*, 1894, 15, 627; *J.C.S.*, 1895, 68 (1), 384. J. Freika and F. Balas, *Spray Prod. Fak. Masar. Univ.*, 1923, 29, 3; *Chem. Abs.*, 1925, 19, 2344. W. Fahrion, *Z. angew. Chem.*, 1907, 20, 356; *J.S.C.I.*, 1907, 26, 264. G. Dupont and J. Levy, *Compt. rend.*, 1929, 189, 763, 920; *Chem. Abs.*, 1930, 24, 855, 1386; *Bull. soc. chim.*, 1930, 47, 147; *Chem. Abs.*, 1930, 24, 2945. G. Dupont, J. Levy and J. Allard, *Bull. soc. chim.*, 1930, 47, 942; *Chem. Abs.*, 1931, 25, 2633. G. Dupont and J. Allard, *Bull. soc. chim.*, 1930, 47, 1216; *Chem. Abs.*, 1931, 25, 3230. G. Rouin, *Bull. inst. pin.*, 1930, 155; *Brit. Chem. Abs.* A, 1931, 227. G. Dupont and J. Dubourg, *Bull. inst. pin.*, 1928, 52, 205; *Chem. Abs.*, 1928, 22, 4839. See also P. Levy, *Ber.*, 1926, 59, 1302; *Chem. Abs.*, 1926, 20, 3012.

<sup>114</sup> I. R. Morozov, *J. Chem. Ind (Moscow)*, 1932 (2), 43; (11), 50; *Chem. Abs.*, 1932, 26, 4485; 1933, 27, 2589. *J. Applied Chem. (U. S. S. R.)*, 1931, 4, 661; *Chem. Abs.*, 1932, 26, 1140. For primers, see also G. S. Baitsukov, *J. Appl. Chem. Russ.*, 1934, 7, 770; *Brit. Chem. Abs.* B, 1935, 160.

<sup>115</sup> I. R. Koehler, Swedish P. 53,760, 1923; *Chem. Abs.*, 1923, 17, 3423.

<sup>116</sup> E. Claxton, British P. 305,656, 1928, to Armstrong Cork Co.; *Chem. Abs.*, 1929, 23, 4837. Canadian P. 305,126, 1930; *Chem. Abs.*, 1931, 25, 835. See also British P. 338,965 and 338,978, 1928; *Chem. Abs.*, 1931, 25, 2581.

<sup>117</sup> A. B. Craven, U. S. P. 1,751,724, Mar. 25, 1930; *Chem. Abs.*, 1930, 24, 2623. British P. 278,922, 1927, to Yorkshire Dyeware & Chem. Co., Ltd.; *Brit. Chem. Abs.* B, 1927, 948. See also A. B. Craven and C. S. Bedford, British P. 274,300, 1926, and 274,722, 1927, to Yorkshire Dyeware & Chem. Co., Ltd.; *Chem. Abs.*, 1928, 22, 2072, 2282.

<sup>118</sup> J. Ternoukov, *Bull. inst. pin.*, 1931, 103; *Brit. Chem. Abs.* B, 1931, 768. A. Tschirch, *Chem. Umshau.*, 1925, 32, 29; *Chem. Abs.*, 1925, 19, 1557.

<sup>119</sup> H. A. Winkelmann, U. S. P. 1,841,235, Jan. 12, 1932, to Phila. Rubber Works Co.; *Chem. Abs.*, 1932, 26, 1832. See also L. P. Rankin (U. S. P. 1,886,586, Nov. 8, 1932, to Hercules Powder Co.;

Rosin was hardened by Low<sup>120</sup> by treatment with formaldehyde under pressure. This treatment applies also to other natural resins such as Manila copal and dammar gum. The method employed is to place rosin and 40 per cent formaldehyde solution in a closed reaction-vessel and then heat the mixture. An alternative procedure is to place rosin in a closed vessel and lead into the container vapors of formaldehyde and steam. The best results are obtained with 2-6 hours heating at 120-150°C. under 75-150 pounds pressure. The condensation of rosin and of other resins with formaldehyde was carried out in alcoholic solution by Lingner,<sup>121</sup> using an acid catalyst, e.g., hydrochloric, sulphuric, formic or acetic acid. As an example rosin (1 part) is dissolved in 4 parts of alcohol and mixed with 1 part of 40 per cent formaldehyde solution. Then hydrochloric acid is introduced into the mixture, causing the precipitation of the condensation product. This product has a higher melting point than the original rosin. The condensation of rosin with aldol or with crotonaldehyde using an acid condensing agent and a solvent such as benzene, carbon tetrachloride or trichloroethane was suggested by Balle and Giloy.<sup>122</sup>

Rosin can be condensed with aldehydes and ketones in the presence of alkalis, alkali sulphides or alkali carbonates.<sup>123</sup> Similarly Voss<sup>124</sup> condensed oxidized rosin with aldehydes. For instance, 200 parts of rosin are oxidized with oxygen under pressure at 100-200°C. and then mixed with 70 parts of formaldehyde and 40 parts of concentrated sodium hydroxide solution at 90-100°C. The mixture is heated 6-8 hours at 160°C. and then poured into a dilute alkaline solution, filtered and cooled. The product is precipitated with hydrochloric acid and then washed and dehydrated.

Boorne and Budde<sup>125</sup> suggested the use of metal oxides or hydroxides as catalysts in the condensation of rosin and aldehydes to form a product for molding articles.<sup>126</sup> In one instance rosin is condensed with formaldehyde using calcium oxide as catalyst, and the reaction product is mixed with sawdust, portland cement, petroleum and calcium carbonate.<sup>127</sup>

Amann<sup>128</sup> condensed formaldehyde and rosin by heating them together at temperatures below 135°C. (usually 110-120°C.) and then modified the product by treating it with phenol or by melting together a phenol-aldehyde resin and the rosin-formaldehyde resin.

A process for simultaneously bleaching and hardening dark-colored rosin was devised by Stuhlmann.<sup>129</sup> The rosin is dissolved in a cold, dilute alkali solution

*Chem. Abs.*, 1933, 27, 1528) on the oxidation of pine oil, and German P. 499,455, 1930 (to Vanillin-Fabrik GmbH, *Chem. Abs.*, 1930, 24, 4121) on the oxidation of cedar-wood oil. A discussion of the use of oxidized turpentine in paints is given by F. L. Browne (*Ind. Eng. Chem.*, 1931, 23, 868, 1214).

<sup>120</sup> F. S. Low, U. S. P. 1,243,312, Oct. 16, 1917, *Chem. Abs.*, 1918, 12, 233. Natural resins such as aceroides gum or gum benzoin are hardened by similar treatment (British P. 225,944, 1923, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1925, 19, 1784). See also German P. 489,920, 1926, to Firma L. Blumer; *Chem. Abs.*, 1930, 24, 2218. Gum aceroides, hardened with formaldehyde or hexamethylenetetramine, has been suggested as a bonding agent in making abrasive materials. See E. E. Novotny, U. S. P. 1,909,784, May 16, 1933, to J. S. Stokes, *Chem. Abs.*, 1933, 27, 3795.

<sup>121</sup> K. A. Lingner, German P. 203,847, 1904, addn. to 183,185, 1904; *Chem. Zentr.*, 1907, 1, 1560; 1908, 2, 1706. British P. 6843, 1907; *J. S. C. I.*, 1907, 26, 1163.

<sup>122</sup> G. Balle and F. Giloy, German P. 406,530, 1922, to Farb. v. m. Meister, Lucius & Brunnig; *J. S. C. I.*, 1925, 44, 461B.

<sup>123</sup> German P. 389,241, 1920, to Plauson's Forschungsinst. GmbH.; *J. S. C. I.*, 1924, 43, 434B. A similar treatment of waxes and bitumens yields viscous products useful as lubricants or salves (British P. 186,950, 1921, to Plauson's, Ltd.; *Chem. Abs.*, 1923, 17, 1160).

<sup>124</sup> A. Voss, German P. 473,411, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 3114.

<sup>125</sup> W. H. Boorne and C. C. L. G. Budde, British P. 247,620, 1924; *Brit. Chem. Abs. B*, 1926, 374.

<sup>126</sup> A. Chwala (German P. 456,351, 1923, *Brit. Chem. Abs. B*, 1930, 430) proposed a similar treatment of fats and waxes.

<sup>127</sup> W. H. Boorne, U. S. P. 1,910,318, May 23, 1933; *Chem. Abs.*, 1933, 27, 4042. British P. 345,472, 1930; *Chem. Abs.*, 1933, 27, 382.

<sup>128</sup> A. Amann, U. S. P. 1,658,828, Feb. 14, 1928, to Chem. Fabr. Dr. K. Albert GmbH.; *Chem. Abs.*, 1928, 22, 1486.

<sup>129</sup> P. Stuhlmann, U. S. P. 1,809,738, June 9, 1931; *Chem. Abs.*, 1931, 25, 4423. British P. 289,859, 1928, to C. Cordes A.-G.; *Brit. Chem. Abs. B*, 1929, 826.



which is kept in continuous motion by a stirring device. The bleaching agent and the aldehyde are then added, reaction taking place in the cold. The product was suggested for sizing paper. The condensation of rosin with a primary aromatic amine yields a product said to be useful as a vulcanization accelerator.<sup>130</sup> An adhesive for fastening rubber to metal or glass is made by condensing aldehydes with the resins from balata or gutta-percha.<sup>131</sup>

The condensation of colophony with phenols in acid solution yields yellow- to brown-colored resins insoluble in water but soluble in alkaline solutions. The sulphonation of these products and conversion into alkali salts yields water-soluble tanning agents.<sup>132</sup> As an example 30 parts of rosin and 15 parts of phenol are heated with 1.5 parts of sulphuric acid (specific gravity 1.7) for 8 hours at 70-80°C. The resulting condensation product is dissolved in carbon tetrachloride and sulphonated with sulphuric acid monohydrate at 10°C. The sulphonated mass is dissolved in hot water and then salted out.

The halogenation of rosin produces a hardening effect but at the same time renders it insoluble in petroleum ether.<sup>133</sup> The chlorinated product is soluble in benzene, alcohol and turpentine, however. To form a product containing 5.5 per cent chlorine, a solution of 200 parts of rosin in 2000 parts of an alkaline solution (containing 19.5 parts sodium hydroxide) is treated with 40 parts of chlorine. The precipitated resin is filtered off, washed and dried. One of the uses for chlorinated rosin is as a soldering flux.<sup>134</sup>

Many methods have been devised by Auer for modifying the properties of rosin and similar substances to form materials for use in varnishes, linoleum and rubber substitutes. In one of these<sup>135</sup> rosin is dissolved in an organic solvent and heated with an electrolyte. Further modification is brought about by vulcanization with sulphur or a sulphur compound. In another method rosin is heated under reduced pressure with a modifying agent consisting of a small proportion of formic acid mixed with such salts as ammonium iodide, sodium sulphide, zinc carbonate or magnesium sulphate.<sup>136</sup> Alkaline oxides or hydroxides are dissolved in rosin and treated with peroxides in one procedure<sup>137</sup> and in a further procedure rosin is heated with sulphur chlorides or sulphonic acids.<sup>138</sup>

Hardened natural resins have been used in a great many ways, only a few of which are mentioned here. The use of hardened rosin as a substitute for copal in plastics of sulphur and resin was suggested by Kissel.<sup>139</sup> A binding medium for roofing is formed by mixing hardened rosin with rosin oil or a heavy mineral oil and adding fillers and waxes.<sup>140</sup> An insulating material can be made from a mixture of creosote oil (8-12 parts), shellac (8 parts), rosin (4 parts), alum (0.5 part) and various amounts of asbestos, magnesium carbonate and calcium hydrox-

<sup>130</sup> W. L. Semon, U. S. P. 1,886,310, Nov. 1, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 1546. See H. A. Morton, U. S. P. 1,784,703, Dec. 9, 1930, *Chem. Abs.*, 1931, 25, 438.

<sup>131</sup> French P. 726,236, 1931, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1932, 26, 4981.

<sup>132</sup> A. Doser and A. Thause, U. S. P. 1,788,371 and 1,788,372, Jan. 13, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4109. German P. 536,170, 1927; *Chem. Abs.*, 1932, 26, 1143. See also British P. 302,938 and 321,190, 1928; *Brit. Chem. Abs. B.*, 1930, 410, 941.

<sup>133</sup> L. Rosenthal, German P. 514,151, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1400.

<sup>134</sup> H. B. Dykstra, U. S. P. 1,785,115, Dec. 16, 1930, to Grasselli Chem. Co.; *Chem. Abs.*, 1931, 25, 484.

<sup>135</sup> L. Auer, British P. 287,943, 1926; *Brit. Chem. Abs. B.*, 1928, 398. Swiss P. 130,435, 1926; *Chem. Abs.*, 1929, 23, 3713. Austrian P. 20,825, 1929; *Chem. Zentr.*, 1930, 2, 3342.

<sup>136</sup> L. Auer, British P. 321,727, 1928; *Brit. Chem. Abs. B.*, 1930, 652. See also British P. 321,724 and 321,725, 1928; *Chem. Abs.*, 1930, 24, 2904, and French P. 694,340, 1930; *Chem. Abs.*, 1931, 25, 1840.

<sup>137</sup> L. Auer, British P. 321,690, 1928; *Brit. Chem. Abs. B.*, 1930, 67. French P. 653,435, 1928; *Chem. Abs.*, 1929, 23, 3821. Hungarian P. 106,463, 1933; *Chem. Abs.*, 1933, 27, 4044. See also British P. 289,414, 1928; *Brit. Chem. Abs. B.*, 1929, 806. Hungarian P. 100,392, 1928; *Chem. Abs.*, 1930, 24, 5517.

<sup>138</sup> L. Auer, U. S. P. 1,980,367, Nov. 13, 1934; *Chem. Abs.*, 1935, 29, 366. British P. 337,739 and 337,750, 1929; *Chem. Abs.*, 1931, 25, 2312.

<sup>139</sup> A. K. Kissel, British P. 4918, 1886, to O. Imray, *J. S. C. I.*, 1887, 6, 219.

<sup>140</sup> H. D. Murray, British P. 382,004, 1931, to Ragusa Asphalte Paving Co., Ltd.; *Brit. Chem. Abs.*, B, 1933, 21.

ide.<sup>141</sup> Another insulating mixture is made from linseed oil, copal, zinc oxide and sulphur.<sup>142</sup> This mixture is exposed to the air 5-9 days and then molded and baked at 50-120°C. Shellac which has become infusible and alcohol-insoluble is reconditioned for use in varnishes and adhesives by mixing it with rosin at 270°C.<sup>143</sup> A composition stated to be a good shellac-substitute was obtained by Dietz and Oeffinger<sup>144</sup> by heating a mixture of batu gum (18-20 parts) and rosin (10-20 parts) with quicklime (1-4 parts) at 260°C. A water-resistant cement for tools is made by fusing hardened rosin with neutral resins and fillers.<sup>145</sup> For making artificial stone or cellular concrete, rosin is mixed with casein or glue and with a cementitious material to produce a foam and then allowed to set.<sup>146</sup>

A molding material is formed by mixing powdered rosin with gasoline or other petroleum fractions and adding milk of lime.<sup>147</sup> The solid product is molded under pressure and is hardened by immersion in water containing gallic acid. For preparing an insoluble product which is resistant to a high temperature and is moldable, shellac was heated at 120-280°C. with 7-10 parts of zinc oxide.<sup>148</sup> A gelatinous material suggested as a belt dressing is formed by mixing kerosene with the reaction product of lime, rosin, formaldehyde, ammonia and chlorinated lime and neutralizing with acetic acid.<sup>149</sup> An artificial asphalt is made by mixing together rosin, shellac, lampblack and a wax.<sup>150</sup> Rosin mixed with montan wax, gilsonite and other materials including fibers forms a box-toe composition.<sup>150</sup>

Banner<sup>151</sup> prepared a linseed-oil substitute by dissolving rosin in a solvent and saponifying it with 18 per cent (of the weight of rosin) of potassium or sodium hydroxide. A turpentine substitute was prepared by Odom<sup>152</sup> by heating rosin with 10 per cent of its weight of calcium oxide for 2 hours at 190°C. and then adding a petroleum distillate and distilling the mixture. Shine<sup>153</sup> made a paint containing a natural resin and old rubber as follows: The scrap rubber is devulcanized, fused and mixed with fused resin and hydrated lime. The mixture is treated with a rubber solvent and with about 10 per cent of its weight of zinc sulphate.

### ROSIN OIL

The destructive distillation of rosin yields a viscous oil known as rosin oil, which is used in the manufacture of lubricants, printing inks, varnishes, cable insulation, oilcloth and linoleum, transformer oils, brewer's pitch and similar materials.<sup>154</sup> The commercial preparation of rosin oil has been described by Grotlich.<sup>155</sup>

<sup>141</sup> H. C. Tazewell, U. S. P. 1,190,814 and 1,190,815, July 11, 1916; *Chem. Abs.*, 1916, 10, 2286.

<sup>142</sup> L. E. Barringer, U. S. P. 1,085,102, Jan. 27, 1914, and 1,111,430, Sept. 22, 1914; *Chem. Abs.*, 1914, 8, 1063, 2536.

<sup>143</sup> R. W. Aldis, *Indian Lac. Res. Inst. Research Notes*, 1933, 7, 1; *Brit. Chem. Abs. B*, 1933, 399.

<sup>144</sup> J. B. Dietz and E. F. Oeffinger, U. S. P. 1,942,413, Jan. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1879. Canadian P. 346,340 and 346,341, 1934, to Canadian Industries, Ltd.; *Chem. Abs.*, 1935, 29, 2276.

<sup>145</sup> German P. 284,701, 1913, to Cefka-G.m.b.H.; *Chem. Abs.*, 1916, 10, 396.

<sup>146</sup> J. A. Rice, U. S. P. 1,788,592, Jan. 13, 1931, and 1,807, 810, June 2, 1931, to the Bubblestone Co.; *Chem. Abs.*, 1931, 25, 1055, 4379.

<sup>147</sup> R. Holtmann, French P. 695,194, 1929; *Chem. Abs.*, 1931, 25, 2556.

<sup>148</sup> W. A. Boughton, U. S. P. 1,933,951, Apr. 10, 1934, to New England Mica Co.; *Chem. Abs.*, 1934, 28, 3920.

<sup>149</sup> H. Behm, U. S. P. 1,812,885, July 7, 1931; *Chem. Abs.*, 1931, 25, 5302.

<sup>150</sup> A. S. Yankelevich, Russian P. 29,175, 1931; *Chem. Abs.*, 1933, 27, 4072.

<sup>151</sup> A. L. Clapp, U. S. P. 1,765,861, June 24, 1930, and 1,790,796, Feb. 3, 1931, to Beckwith Mfg. Co.; *Chem. Abs.*, 1930, 24, 4129; 1931, 25, 1646. U. S. P. 1,544,818 and 1,544,814, July 7, 1925; *Chem. Abs.*, 1925, 19, 2731.

<sup>152</sup> S. Banner, British P. 29,728, 1897; *J.S.C.I.*, 1898, 17, 1158.

<sup>153</sup> L. L. Odom, U. S. P. 1,625,622, Apr. 19, 1927, to M-O-R Products Co.; *Chem. Abs.*, 1927, 21, 2073.

<sup>154</sup> G. A. Shine, U. S. P. 1,583,150, June 8, 1926; *Chem. Abs.*, 1926, 20, 2589.

<sup>155</sup> It may be of interest to note the results of the destructive distillation of other resins, for instance the copals. See A. H. Gill and D. Nishida, *Ind. Eng. Chem.*, 1923, 15, 1276, and H. Wolff, *Farben-Ztg.*, 1924, 29, 2039; *J.S.C.I.*, 1924, 43, 952B.

<sup>156</sup> V. E. Grotlich, *Proc. Am. Soc. Testing Materials*, 1930, 30(2), 834; *Chem. Abs.*, 1931, 25, 2309. See also H. Hadert, *Farben-Chem.*, 1934, 5, 130; *Chem. Abs.*, 1934, 28, 3603.

The distillation is carried out in cast-iron or steel stills holding 6500-12,000 pounds of rosin. The darker grades of rosin are usually employed. Water is first evolved (at about 120°C.), then various fractions of rosin oil are collected. These fractions are rosin spirits (pinohn) (160°C.), light oil (200°C.), kidney oil (250°C.) and bloom oil (270°C.). Distillation is stopped at 360°C., leaving a residue of rosin pitch. Kidney oil, the most valuable fraction, is used principally in greases and printing inks. Because of its acid content (40-56 per cent) the kidney oil is converted partially into soaps when used in greases.

One of the early methods of rosin oil production consisted in heating rosin in an iron autoclave at 250-260°C. under 12-15 atmospheres pressure.<sup>166</sup> In one of the modern methods rosin is heated at 150-325°C. (300°C. is considered best) with 2 per cent of a siliceous earth or of activated carbon, yielding a neutral rosin oil.<sup>167</sup>

Binapff<sup>168</sup> used in a similar process a catalyst composed of an aluminum hydro-silicate activated with hydrochloric acid. To illustrate, 500 parts of rosin are heated with 25 parts of catalyst to a temperature of 180-200°C. in one hour. Heating is continued for another hour at 215-220°C. When the evolution of gases has ceased the temperature is raised to 240-250°C. for 20 minutes. The catalyst is removed by filtration and the product is distilled *in vacuo* yielding a clear, yellowish oil (boiling 70-390°C.) and leaving a small amount of pitchy residue. The oil is substantially neutral (acid value less than 1), consisting mainly of hydrocarbons.

In a process devised by Hoge<sup>169</sup> rosin is subjected to a vapor-phase cracking at 370-590°C. under atmospheric pressure to yield liquid products. Aluminum is used as the catalyst in the cracking. Fractionation of the liquid products yields materials for various uses. For instance, a fraction from 75-160°C. is used as a gum solvent in lacquer manufacture and one from 190-250°C. is proposed as a plasticizer in lacquers. A light, oily product said to be useful in paints is obtained by heating a rosin and water mixture to above 480°C. so that a vapor pressure of 5000 pounds per square inch is produced.<sup>160</sup>

Johnston<sup>161</sup> obtained a drying oil (b.p. 340-360°C.) by heating rosin with benzenesulphonic acid at 250-300°C. and removing the oil by distillation. The product is rendered neutral by redistilling from dilute sodium carbonate solution.

The distillation of rosin or other natural resins with 1-5 per cent of phosphoric acid up to 310°C. yields a light oil (50 per cent yield) useful as a turpentine substitute. The still-residue is a neutral rosin oil of low viscosity.<sup>162</sup> In other methods of rosin-oil production, rosin is distilled with boric acid or a borate<sup>163</sup> (0.05-1.0 per cent) or with zinc chloride.<sup>164</sup>

Some idea of the nature of rosin oil formation can be obtained from the studies

<sup>166</sup> P. Huth and W. Lippert, *Chem. Rev. Fett-u. Harz-Ind.*, 1902, 9 (10), 226; *J.S.C.I.*, 1902, 21, 1336.

<sup>167</sup> I. W. Humphrey, U. S. P. 1,852,244, April 5, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1932, 26, 3103.

<sup>168</sup> J. Binapff, U. S. P. 1,952,233, Mar. 27, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3605. British P. 372,402, 1931; *Brit. Chem. Abs. B.*, 1932, 737. German P. 572,474, 1930; *Chem. Abs.*, 1933, 27, 3095. French P. 720,856, 1931; *Chem. Abs.*, 1932, 26, 4191.

<sup>169</sup> D. W. Hoge, U. S. P. 1,902,073, Mar. 21, 1933, to C. W. Newbery; *Chem. Abs.*, 1933, 27, 3350.

<sup>160</sup> G. Egloff and H. P. Benner, U. S. P. 1,783,230, Dec. 2, 1930, to Universal Oil Prod. Co.; *Chem. Abs.*, 1931, 25, 424.

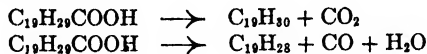
<sup>161</sup> A. C. Johnston, U. S. P. 1,975,211, Oct. 2, 1934, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 7561.

<sup>162</sup> J. M. A. Chevalier, P. Bourcet and H. Regnault, U. S. P. 1,572,766, Feb. 9, 1926; *Chem. Abs.*, 1926, 20, 1331.

<sup>163</sup> J. N. Borglin, U. S. P. 1,782,401, Nov. 25, 1930, to Hercules Powder Co.; *Chem. Abs.*, 1931, 25, 424.

<sup>164</sup> R. C. Palmer, U. S. P. 1,660,762, Feb. 28, 1928; *Chem. Abs.*, 1928, 22, 1486.

of Easterfield and Bagley,<sup>165</sup> Ruzicka and Schinz<sup>166</sup> and La Lande.<sup>167</sup> An unsaturated hydrocarbon,<sup>168</sup> abietene, results from the decarboxylation of abietic acid by one of the following reactions:



The sulphonation of abietene yields a product useful as a wetting agent.<sup>169</sup> Abietenesulphonic acid is a black paste soluble in water in all proportions, and its sodium salt, which is usually employed as the wetting agent, is described as a tan-colored powder.

Products for varnishes can be obtained by the oxidation of rosin oil.<sup>170</sup> An oil boiling above 200°C. is treated under reflux with a current of air containing 10-15 per cent of superheated steam until it becomes nearly solid. Distillation of the product yields 20-30 per cent of unchanged oil, 30-40 per cent of heavy rosin oil and 30-40 per cent of black pitch. Bedford and Bedford<sup>171</sup> oxidized rosin oil to a viscous mass useful in linoleum manufacture. It has been reported, however, that a very brittle product results when this is used.<sup>172</sup>

#### RESINS FROM TERPENES

Turpentine, pine oil and related materials are potential raw materials for synthetic resins and can be considered here since they are derived from the same source as rosin. The principal constituent of turpentine is a terpene, pinene, and of pine oil is a mixture of terpene alcohols (largely  $\alpha$ -terpineol) with small amounts of terpene hydrocarbons and ethers.<sup>173</sup> As has been mentioned previously, pine oil is obtained by steam-distillation of pine wood. In addition to the recovery of pine oil and turpentine in this process other terpene hydrocarbons such as limonene, dipentene, terpinene and terpinolene are also obtained as intermediate fractions.<sup>174</sup>

The principal methods for producing resinous materials from these substances are by oxidation or by polymerization. In fact turpentine tends to resinify during storage, probably because of oxidation.<sup>175</sup> The evaporation of turpentine and pine oils in open vessels yields resinous materials as a result of oxidation and polymerization.<sup>176</sup> Thickened turpentine obtained in this manner is known commercially as

<sup>165</sup> T. H. Easterfield and G. Bagley, *J.C.S.*, 1904, 85, 1238. See also P. Levy, *Ber.*, 1906, 39, 3043; *Chem. Abs.*, 1907, 1, 54.

<sup>166</sup> L. Ruzicka and H. Schinz, *Helv. Chim. Acta*, 1923, 6, 833; *Chem. Abs.*, 1924, 18, 248.

<sup>167</sup> W. A. La Lande, Jr., *Ind. Eng. Chem.*, 1934, 26, 678.

<sup>168</sup> Other hydrocarbons have, of course, been found in rosin oil. See A. Renard, *Bull. soc. chim.*, 1881, (2) 36, 215; *J.C.S.*, 1882, 42, 64; *Compt. rend.*, 1887, 105, 865; 1888, 106, 856, 1086; *J.C.S.*, 1888, 54, 161, 731, 846. W. A. Tilden, *Ber.*, 1880, 13, 1604, *J.C.S.*, 1881, 40, 101. W. Smith, *J.C.S.*, 1878, 30, 29. W. Schultze, *Ann.*, 1908, 359, 129; *Chem. Abs.*, 1908, 2, 1715. P. Levy, *Ber.*, 1906, 39, 3043; *J.C.S.*, 1906, 90 (1), 870. S. Imori and T. Isono, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 1928, 7, 89; *Chem. Abs.*, 1928, 22, 3307.

<sup>169</sup> I. Gubelmann, H. J. Weiland and C. O. Henke, *Ind. Eng. Chem.*, 1931, 23, 1462. C. O. Henke, U. S. P. 1,833,353, Apr. 12, 1932, to Newport Industries, Inc.; *Chem. Abs.*, 1932, 26, 3372. British P. 368,293, 1930, to Newport Chem. Corp.; *Brit. Chem. Abs. B*, 1932, 495. French P. 710,541 and 710,915, 1931; *Chem. Abs.*, 1932, 26, 1803, 1797.

<sup>170</sup> G. Ruth and E. Asser, German P. 336,253, 1920; *J.S.C.I.*, 1921, 40, 595A.

<sup>171</sup> J. E. Bedford and C. S. Bedford, British P. 7742, 1893, and 29,656, 1897; *J.S.C.I.*, 1894, 13, 406; 1898, 17, 1158.

<sup>172</sup> F. Frits, *Farben-Ztg.*, 1923, 29, 184; *Chem. Abs.*, 1925, 19, 185.

<sup>173</sup> See R. C. Palmer, *Ind. Eng. Chem.*, 1934, 26, 703. O. A. Pickett and J. M. Schantz, *ibid.*, 707.

<sup>174</sup> Reports on the properties and composition of wood turpentine are given by L. F. Hawley (*Reports 8th Int. Cong. Applied Chem.*, 1912, 12, 41) and by C. A. Lambert (*Ind. Eng. Chem.*, 1923, 14, 491). The properties of pine-oil constituents are given by R. H. Stevens (*Chem. Met. Eng.*, 1922, 26, 629).

<sup>175</sup> J. Terpougoft, *Bull. inst. pin.*, 1928, 48, 103; *Chem. Abs.*, 1928, 22, 3262. W. C. Smith and H. P. Holman, *Ind. Eng. Chem.*, 1934, 26, 716.

<sup>176</sup> H. A. Gardner, *Paint Mfrs. Assoc. of U. S. Circ.*, 1923, 163, 106; *Chem. Abs.*, 1923, 17, 1841. For notes on the polymerisation of pinene see I. Kondakov and S. Saprikin, *Bull. soc. chim.*, 1925, (4) 37, 1045; *J.C.S.*, 1925, 128 (1), 1292.

"fat oil." Experiments performed by Horton and McCormick<sup>177</sup> on laboratory-made fat oil indicated that the oil can be used in cellulose lacquers in amounts up to 25 per cent. It was stated that hard films of high natural gloss and of satisfactory resistance to steam and ultraviolet light are obtained with such lacquers.

Gardner<sup>178</sup> polymerized turpentine to obtain a paint vehicle which forms a hard surface on drying. In the procedure turpentine or pine oil (100 parts) is heated at 80-160°C. with 92 per cent sulphuric acid (5-7.5 parts). The polymerization of turpentine hydrocarbons with sulphuric acid yields substances suggested for use in the rubber and varnish industries.<sup>179</sup> The acid is stirred into the oil of turpentine until 20 per cent of the mixture is acid and then heat is applied. The method may be varied somewhat by adding 5-10 per cent of potassium dichromate to the acid.

The conversion of turpentine and pine oils into heavy paint-vehicles was carried out by Smith<sup>180</sup> by refluxing the oil in contact with fuller's earth. The earth is placed between the still and the reflux condenser so that both the vapors and the returning condensate will come in contact with it. The polymerization of turpentine can be effected by prolonged heating either alone or with aluminum chloride, aluminum bromide or zinc chloride.<sup>181</sup> Cooper<sup>182</sup> obtained a drying oil by treating a turpentine solution with aluminum chloride at 30°C. and distilling the product under reduced pressure.

Various methods were used by Humphrey<sup>183</sup> to polymerize turpentine, pine oil and dipentene. In one of them the vapors of pine oil are brought into contact with fuller's earth for 8 hours at 160-170°C. In another process dipentene vapors are passed in intimate contact with fuller's earth, aluminum oxide or chlorides of zinc, tin, aluminum or iron at 400°C. The oils themselves are heated with fuller's earth or metallic chlorides in other procedures. A turpentine substitute is made by heating pine oil with iodine and then steam-distilling. To produce a rapidly drying oil, a polymerized terpene product from turpentine, pine oil or dipentene is distilled to remove the fraction boiling below 335°C. so that only polymers higher than the diterpene are retained.<sup>184</sup>

A drying-oil substitute can be prepared by heating pine-tar with salts of lead, manganese or copper to above 150°C. and then diluting the product with an organic solvent.<sup>185</sup> To form a binder for printing inks polymerized terpenes are mixed with boiled wood oil.<sup>186</sup> Another use of polymerized terpenes is in the formation of adhesives by mixing them with natural gums.<sup>187</sup>

It has already been mentioned that the oxidation of turpentine and pine oil causes resinification.<sup>188</sup> Pellnitz<sup>189</sup> resinified pine oil by adding to it 1 per cent of acetic or resin acid and treating with moist, ozone-containing air under pressure.

<sup>177</sup> P. M. Horton and W. F. McCormick, *Ind. Eng. Chem.*, 1934, 26, 1226.

<sup>178</sup> H. A. Gardner, U. S. P. 1,370,106, Mar. 1, 1921; *Chem. Abs.*, 1921, 15, 1630.

<sup>179</sup> E. A. L. Rouzeville and P. A. M. Creuzillet, French P. 639,726, 1927; *Chem. Abs.*, 1929, 23, 722.

<sup>180</sup> E. B. Smith, U. S. P. 1,784,949, Dec. 16, 1930, to E. W. Colledge (for National Turpentine Products Co.); *Chem. Abs.*, 1931, 25, 609.

<sup>181</sup> O. Routala and O. Kuula, *Teknill. Aikak.*, 1932, 22, 347; *Chem. Abs.*, 1932, 26, 5747; *Soumen Kem.*, 1932, 5, 52; *Brit. Chem. Abs. B*, 1932, 996.

<sup>182</sup> S. M. Cooper, U. S. P. 1,938,320, Dec. 5, 1933, to Gulf Refining Co.; *Brit. Chem. Abs. B*, 1934, 895.

<sup>183</sup> I. W. Humphrey, U. S. P. 1,691,065, 1,691,066, 1,691,067, 1,691,068, 1,691,069 and 1,691,573, Nov. 13, 1928, to Hercules Powder Co.; *Chem. Abs.*, 1929, 23, 510.

<sup>184</sup> I. W. Humphrey, U. S. P. 1,793,220, Feb. 17, 1931, to Hercules Powder Co.; *Chem. Abs.*, 1931, 25, 2311.

<sup>185</sup> M. M. Chilikin, Russian P. 164, 1922; *Chem. Abs.*, 1933, 27, 4428.

<sup>186</sup> E. Strasser, French P. 743,787, 1933, to N. V. Handelsmaatschappij "Baver"; *Chem. Abs.*, 1933, 27, 4107.

<sup>187</sup> A. R. Kemp, U. S. P. 1,832,031, Oct. 11, 1932, to Bell Telephone Labs., Inc.; *Chem. Abs.*, 1933, 27, 545.

<sup>188</sup> See V. V. Shkatelov, *Mem. inst. agron. et forest. etat Bélarussie*, 1925, 5, 9; *Chem. Abs.*, 1930, 24, 3352.

<sup>189</sup> O. P. Pellnitz, German P. 202,254, 1907; *Chem. Abs.*, 1909, 3, 494.

The product formed is treated with quicklime and steam-distilled. The oxidation of turpentine with air or oxygen in the presence of a catalyst produces a fatty essence.<sup>190</sup> A drying oil which may be used as a substitute for linseed oil was made by Rankin<sup>191</sup> by treating dipentene with ozone at temperatures below 110°C. Heating the product to 120°C. increases its solvent power for nitrocellulose but decreases its drying power. Another drying oil is obtained by first polymerizing turpentine oil or dipentene by refluxing it with sulphuric acid or stannic chloride and then treating the product with ozonized air.<sup>192</sup>

Humphrey<sup>193</sup> produced an oil capable of assisting the dissolving of nitrocellulose by treating pine oil with a dehydrating agent and then oxidizing the product. The object of the dehydration is to convert terpineols into lower-boiling substances thus giving greater volatility and better solvent action to the oil. As an example pine oil is heated with 1.5 per cent of fuller's earth for 1 hour at 145°C. The earth is removed and the oil is fractionally distilled. The higher-boiling fraction is oxidized with nitric acid, chromic acid, chlorine or other agents and then mixed with the lower-boiling fraction. From 1 to 20 per cent of this product is incorporated in nitrocellulose lacquers.

Resins were produced by Orlov<sup>194</sup> by condensing turpentine with formaldehyde. As an example 200 parts of sulphuric acid (specific gravity 1.84) are mixed slowly with 100 parts of turpentine. To this are added 55-65 parts of 40 per cent formaldehyde solution at a temperature below 40°C. The mixture is allowed to stand for 12 hours and is then neutralized with ammonium hydroxide, producing a green coloration. The aqueous layer is removed, the residue is given a further treatment with ammonium hydroxide and the mixture is heated to boiling and then allowed to cool. The resin obtained (80 per cent yield) by filtration and drying (70-80°C) is yellowish brown in color and is soluble in alcohol, ether, benzene, toluene, acetic acid, ethyl acetate and solvent naphtha. Solutions with the last two of these give quick-drying lacquers.

In like manner reaction takes place between pine oil and paraformaldehyde as shown by the following experiment performed in the author's laboratory:

A mixture of 50 grams of pine oil, 15 grams of paraform and 20 cc. of concentrated hydrochloric acid was heated under a reflux condenser. After the paraform had passed into solution an additional quantity of 15 grams was added and the refluxing continued. All of the paraform dissolved but the odor of formaldehyde persisted. The solution became very dark brown in color and considerably thicker. The reaction product did not separate easily from the aqueous acid, hence it was extracted with benzene. After evaporation on the water bath a product of tarry consistency remained. When this was carefully heated to a somewhat higher temperature a portion volatilized and the remainder upon cooling solidified to a brittle brownish-black mass.

Ushakov and Sokolov<sup>195</sup> used the procedure of Orlov to obtain resins from pine oil. Borneol, camphane and pinene, obtained from the oil of Siberian fir, condensed with formaldehyde in the presence of sulphuric acid to yield pitches soluble in benzene. Bornyl and isobornyl chlorides, obtained from the fraction of this oil boiling between 156-162°C., when condensed with formaldehyde using ferric chloride or sulphuric acid as a catalyst, produced black or dark-brown resins.

<sup>190</sup> L. Desalbres and J. Dubourg, French P. 620,462, 1926; *Brit. Chem. Abs.* B, 1928, 866.

<sup>191</sup> L. P. Rankin, U. S. P. 1,910,564, May 23, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 4108.

<sup>192</sup> L. P. Rankin, U. S. P. 1,886,586, Nov. 8, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 1528.

<sup>193</sup> I. W. Humphrey, U. S. P. 1,653,009 and 1,653,010, Dec. 20, 1927, to Hercules Powder Co.; *Chem. Abs.*, 1928, 22, 878.

<sup>194</sup> G. Orlov, German P. 191,011, 1906; *J.S.C.I.*, 1908, 27, 234. See E. I. Orlov, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 800; *J.C.S.*, 1908, 94(1), 815.

<sup>195</sup> S. N. Ushakov and A. D. Sokolov, *Zhur. Priklad. Khimii*, 1930, 3, 47; *Chem. Abs.*, 1930, 24, 3796.

Constituents of pine oil were used by Wuyts<sup>196</sup> in condensations with phenols to form resinous products. Catalysts employed included phosphoric, oxalic, sulphuric and halogen acids, chlorides of zinc, aluminum and iron, siliceous earths and halogens. The various products formed were suggested as antiseptics, as electric insulators and in the manufacture of varnishes. An emulsion with water in alkaline solution was found useful for degreasing and cleaning purposes.

As an example of such resin formation, equimolecular proportions of carvene and phenol were mixed with 0.1 per cent of p-toluenesulphonic acid and the temperature was maintained below 105°C. The reaction product was treated with steam and then with caustic soda or potash using toluene as a solvent. In this latter step two layers formed, and from the alkaline layer was recovered the resinous product.

The use of terpinene-maleic anhydride as an adhesive for uniting celluloid or other transparent material to glass in the making of safety glass was suggested by Peters.<sup>197</sup> The compound is produced by the reaction of 480 parts of  $\alpha$ -terpinene with 294 parts of maleic anhydride at 150-200°C. for 5 hours. Impurities are removed by distillation under vacuum (15 mm).

Many miscellaneous experiments with terpenes have yielded resins. For instance, pinene and oxalic acid react to form a large quantity of resin and a small amount of acetic acid.<sup>198</sup> Treatment of pinene with phosphorus pentachloride yields hydrogen chloride, pinene dichloride, phosphorus trichloride, some tar and a dark yellow resin.<sup>199</sup> An adhesive for catching insects has been prepared from chlorinated terpenes.<sup>200</sup> Prolonged contact of turpentine with iron yields small amounts of a clear, red resin.<sup>201</sup> Resinous material is formed in the oxidation of limonene with hydrogen peroxide in acetic acid solution.<sup>202</sup> Citral upon treatment with 50 per cent sulphuric acid yields p-cymene and resinous substances.<sup>203</sup>

Cedrenene,  $C_{15}H_{22}$ , tends to polymerize to an amorphous mass when placed in contact with acetic anhydride or when boiled at ordinary pressure.<sup>204</sup> When linalool is heated with aluminum at 160-205°C. there are formed dipentene (30 per cent), camphor (2 per cent), borneol (0.8 per cent), camphorene (22 per cent) and resin (15 per cent).<sup>205</sup> The treatment of caryophyllene with ethyl diazoacetate yields a cyclopropane ester which on subsequent hydrolysis with concentrated caustic potash forms a resinous acid.<sup>206</sup> Pinocarveol and sabinol, when heated with aluminum alcoholate yield pinocamphone and sabinol tenacetone and resinous material as a by-product.<sup>207</sup> Attempts made by Houben<sup>208</sup> to esterify terpineol, linalool and geraniol by means of magnesium alkyl bromides produced colored halogen-containing esters which quickly resinified.

#### RESINATES AND OTHER METALLIC SOAPS

Although this discussion should adhere strictly to the metallic salts of resin acids, the salts of fatty acids and naphthenic acids will be considered to some extent because of the similarity of their uses. The term "metallic soap" applies

<sup>196</sup> H. Wuyts, U. S. P. 1,469,709, Oct. 2, 1923; *J.S.C.I.*, 1923, 42, 1234A. British P. 204,754, 1922; *Chem. Abs.*, 1924, 18, 911.

<sup>197</sup> G. H. Peters, U. S. P. 1,882,298, Oct. 11, 1932, to Hercules Powder Co; *Chem. Abs.*, 1933, 27, 824. See also Chapter 40.

<sup>198</sup> G. Scagliarini and G. Saladini, *Gazz. chim. ital.*, 1923, 53 (1), 135; *J.C.S.*, 1923, 124 (1), 587.

<sup>199</sup> L. Bert, *Bull. soc. chim.*, 1923, 33, 787; *J.C.S.*, 1923, 124 (1), 812.

<sup>200</sup> A. Thause and H. Kükenthal, German P. 523,218, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3449.

<sup>201</sup> S. I. Levy and R. Defries, *J.S.C.I.*, 1923, 42, 472T.

<sup>202</sup> J. Sward, *J.C.S.*, 1925, 127, 1632.

<sup>203</sup> R. Horinchi, *Mem. Coll. Sci. Kyoto Imp. Univ.*, (A) 11 (3), 171; *Chem. Abs.*, 1928, 22, 3886.

<sup>204</sup> A. Blumann and L. Schulz, *Ber.*, 1931, 64, 1540; *Chem. Abs.*, 1931, 25, 4542.

<sup>205</sup> I. W. Vinogradova, *Ber.*, 1931, 64, 1991; *Chem. Abs.*, 1931, 25, 5896.

<sup>206</sup> D. T. Gibson, *J.C.S.*, 1928, 750.

<sup>207</sup> H. Schmidt, *Ber.*, 1929, 62, 103; *Chem. Abs.*, 1929, 23, 2422.

<sup>208</sup> J. Houben, *Ber.*, 1906, 39, 1736; *J.C.S.*, 1906 90 (1), 520.

generally to the water-insoluble salts and therefore does not include soaps of the alkali metals. These metallic soaps have found extensive use in paints and varnishes, waterproofing materials, greases, emulsifying agents, wetting agents and plastic materials. As driers in paints the soaps of cobalt, manganese and lead are most commonly used.<sup>200</sup>

Metallic soaps are of two types, generally referred to as fused soaps and precipitated soaps. The fused soaps are made by heating free fatty or resin acids with metal oxides, substantially as described in the section on the liming of rosin. Precipitated soaps are prepared by the double decomposition of alkali soaps (sodium, potassium or ammonium) in aqueous or alcoholic solution with aqueous solutions of salts of the other metals.<sup>210</sup> The precipitated soaps are distinctly superior to those made by fusion because when properly prepared they contain a definite percentage of metal which completely saturates the acid employed, whereas the fused soaps are rarely definite in composition and the acid is only partly neutralized.<sup>211</sup> Preference is often given however to the fused soaps because of their ease of preparation.<sup>212</sup> It has been shown that the fused soaps show less tendency to crystallize and precipitate from solution because of their lower metal content.<sup>213</sup>

As has just been mentioned one of the uses for resinsates and other metallic soaps is as drying agents in paints and varnishes.<sup>214</sup> Many explanations of the action of driers have been made. In the modern theory of drier action the driers accelerate the oxidation of oils by neutralizing antioxidants and to a lesser degree accelerate association or polymerization of the oxidized oil molecules. Also, it is conceivable that the driers accelerate gelation of the oil by acting as coagulation nuclei.<sup>215</sup> The results of various investigations show that the most efficient driers

<sup>200</sup> For discussions on the use of metallic soaps see H. I. Jones, *Chem. Met. Eng.*, 1923, 28, 489. R. Wechsler, *Paint, Oil and Chem. Rev.*, 1927, 83 (5), 12, *Chem. Abs.*, 1927, 21, 1192. H. J. Braun, *Metalbörse*, 1929, 19, 1461; *Chem. Abs.*, 1929, 23, 4360. M. F. Lauro, *Oil and Fat Ind.*, 1928, 5, 329; *Chem. Abs.*, 1929, 23, 1004. F. J. Lacata, *Am. Paint J.*, 1931, 15 (38), 68, *Chem. Abs.*, 1931, 25, 4426. Reviews are given by H. N. Bassett, *J.S.C.I.*, 1934, 53, 504, and T. Ruemele, *Paint and Varnish Prod. Mgr.*, 1934, 10 (6), 6; *Brit. Chem. Abs. B*, 1934, 635.

<sup>210</sup> Detailed descriptions of the preparation of metallic soaps are given by H. A. Gardner and R. E. Coleman, *Paint Mfrs. Assoc. of U. S., Circ.*, 1921, 120. See also P. Truchot, *Rev. chim. ind.*, 1897, 8, 107; *J.S.C.I.*, 1897, 16, 449. A. Lavache, *J. pharm. chim.*, 1899, (6) 10 (7), 322, *J.S.C.I.*, 1899, 18, 1134. E. Cadoret and E. Delignon, *French P.* 423,545, 1910; *J.S.C.I.*, 1911, 30, 636. R. F. Uzac, *French P.* 595,497, 1925; *Brit. Chem. Abs. B*, 1926, 414. J. Uthoff, *Quim. e ind.*, 1930, 7, 49, *Chem. Abs.*, 1930, 24, 5520. J. Chabannais, *French P.* 625,219, 1926; *Brit. Chem. Abs. B*, 1928, 792. P. S. Miller, U. S. P. 1,894,113, Jan. 10, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 2591. British P. 350,735, 1930, to British Thomson-Houston Co.; *Brit. Chem. Abs. B*, 1931, 769. J. Alas, *French P.* 744,848, 1933; *Chem. Abs.*, 1933, 27, 4251. G. Kranzlem, R. K. Muller and L. Berlin, *German P.* 569,946, 1933, to I. G. Farbenund. A-G; *Chem. Abs.*, 1933, 27, 3723. British P. 395,406, 1933, to Titanium Pigment Co., Inc.; *Chem. Abs.*, 1934, 28, 669. For the preparation of metal soaps from shellac see W. H. Gardner, W. F. Whitmore and H. J. Harris, *Ind. Eng. Chem.*, 1933, 25, 696. The formation of insoluble shellacates in coating compositions may be prevented by addition of malic acid. W. H. Gardner, U. S. P. 1,918,804, July 18, 1933, to U. S. Shellac Importers Assoc.

<sup>211</sup> Methods of analysis of metallic soaps have been presented by R. Uzac (*Chimie et industrie*, 1925, 14, 186; *Chem. Abs.*, 1925, 19, 3444) and P. Muller, (*Farben-Ztg.*, 1927, 32, 798, 851, *Brit. Chem. Abs. B*, 1927, 147).

<sup>212</sup> Metallic abietates have been prepared and described by G. Dupont and L. Desalbes, *Bull. soc. chim.*, 1926, (4) 39, 492; *Brit. Chem. Abs. A*, 1926, 611 and L. L. Steele, *J.A.C.S.*, 1922, 44, 1333. Other metallic soaps are described by W. F. Whitmore and M. Lauro, *Ind. Eng. Chem.*, 1930, 22, 646.

<sup>213</sup> See *Farben-Ztg.*, 1927, 32, 2020; *Chem. Abs.*, 1928, 22, 1861. Cf., however, A. W. C. Harrison (*Farbe u. Lack*, 1931, 16; *Brit. Chem. Abs. B*, 1931, 356) who states that fused soaps do not always give stable solutions. A. H. Sabin (*Decorator* 1934, 33 (389), 32; *Brit. Chem. Abs. B*, 1934, 971) has observed that fused linoleates are too rapid in their action, causing wrinkling in oil varnishes.

<sup>214</sup> See H. A. Bruson, U. S. P. 1,920,160, July 25, 1933, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1933, 27, 4942. A. J. Ducamp and M. E. A. Baule, *British P.* 383,856, 1932; *Brit. Chem. Abs. B*, 1933, 115. *French P.* 729,547, 1931; *Chem. Abs.*, 1933, 27, 434. F. Wilborn and E. Rieger, *German P.* 583,249, 1933, to Inst. für Lackforschung G.m.b.H.; *Chem. Abs.*, 1934, 28, 351. J. K. Hunt and G. H. Latham, U. S. P. 1,948,582, Feb. 27, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 2926.

<sup>215</sup> See A. C. Elm, *Ind. Eng. Chem.*, 1934, 26, 386. H. N. Stephens, *ibid.*, 1932, 24, 918. Philadelphia Paint Club, *Amer. Paint and Varnish Mfrs. Assoc., Circ.*, 1932, 423; *Chem. Abs.*, 1933, 27, 432; *Paint Manuf.*, 1933, 3, 18, 28, 48, 62; *Brit. Chem. Abs. B*, 1933, 435. A. V. Blom, *Z. angew. Chem.*, 1927, 40, 146; *Chem. Abs.*, 1927, 21, 1720. *Farben-Ztg.*, 1931, 36, 646, 691; *Brit. Chem. Abs. B*, 1931, 210. J. S. Long and H. D. Chataway, *Ind. Eng. Chem.*, 1931, 23, 53. J. S. Long and W. S. W. McCarter, *ibid.*, 1931, 23, 53. H. Ingle, *J.S.C.I.*, 1917, 36, 819. S. Coffey, *J.C.S.*, 1922, 121, 17.



are the soaps of cobalt and manganese. These and the soaps of lead are the most commonly used driers.<sup>216</sup> It has been found that mixtures of metallic soaps produce more rapid drying action than the soaps of any one metal alone.<sup>217</sup> In the opinion of Steele<sup>218</sup> there is practically no advantage in the use of more than 0.05 per cent of either cobalt or manganese to dry linseed oil nor more than 0.05 per cent of lead in combination with 0.01 per cent of manganese or 0.1 per cent of lead with 0.005 per cent of manganese. It has been found that cobalt driers (oleate or resinate) exert a greater influence in causing "skinning" of stored varnishes than do the soaps of lead or manganese.<sup>219</sup> Much has been said about the relative efficiency of various soaps, some workers preferring oleates and linoleates and others advocating resinates.<sup>220</sup>

The use of naphthenates as driers in paints and varnishes has been recommended by various investigators<sup>221</sup> because of their uniformity, stability and better solubility.<sup>222</sup> These compounds, commonly known as Soligen driers, are metallic soaps of naphthenic acids, which are derived from crude petroleum.<sup>223</sup>

In one method of producing naphthenate driers, naphthenic acid is saponified with sodium or potassium hydroxide in a boiling aqueous solution. A salt of a

<sup>216</sup> With special reference to lead soaps see H. Wolff, *Farben-Ztg.*, 1925, 31, 29; *J.S.C.I.*, 1925, 44, 931B. R. Uzac, *Bull. soc. chim.*, 1925, (4) 37, 1194; *J.S.C.I.*, 1925, 44, 931B. C. Coffignier, *Bull. soc. chim.*, 1925, (4) 37, 1078; *Chem. Abs.*, 1925, 19, 3604; *Rev. gen. colloides*, 1926, 4, 1, 65; *Chem. Abs.*, 1926, 20, 2039. S. H. Diggs and F. S. Campbell, *Ind. Eng. Chem.*, 1928, 20, 828. W. Laufenberg, *Farben-Ztg.*, 1929, 35, 546; *Chem. Abs.*, 1930, 24, 1231. M. Ragg, *Farben-Ztg.*, 1929, 34, 1805, 1661; *Brit. Chem. Abs. B*, 1929, 441. K. Charisius and E. Kindscher, *Farben-Ztg.*, 1931, 36, 780, 1297; *Brit. Chem. Abs. B*, 1931, 356, 685. A. V. Blom, *Farben-Ztg.*, 1931, 36, 1045; *Brit. Chem. Abs. B*, 1931, 450. H. A. Gardner, *Amer. Paint, Varnish Mfrs. Assoc., Circ.*, 1931, 377, 133; *Chem. Abs.*, 1931, 25, 2009. W. A. La Lande, Jr., *J.A.C.S.*, 1931, 53, 1858. H. Heberling, *Farbe u. Lack*, 1931, 161; *Chem. Abs.*, 1932, 26, 3123. M. Ragg, *Trans. Electrochem. Soc.*, 1933, 64, 293; *Brit. Chem. Abs. B*, 1933, 927. E. Kindscher and P. Lederer, *Farben-Ztg.*, 1933, 38, 1336; *Brit. Chem. Abs. B*, 1934, 27. C. P. A. Kappelmeier, *Verfkronek.*, 1934, 7, 39; *Chem. Abs.*, 1934, 28, 3915. H. Wolff and J. Rabinowicz, *Fettechem. Umschau*, 1934, 41, 66; *Chem. Abs.*, 1934, 28, 4253. H. Levin, *Ind. Eng. Chem.*, 1934, 26, 333.

With reference to iron soaps see H. Salvaterra, *Z. angew. Chem.*, 1930, 43, 620; *Chem. Abs.*, 1930, 24, 4414. B. C. Soyenko, *J. Phys. Chem.*, 1930, 34, 2519; *Chem. Abs.*, 1931, 25, 245. A. E. Kimberley and J. F. G. Hicks, *Bur Standards J. Research*, 1931, 6, 819; *Chem. Abs.*, 1931, 25, 5989. H. Salvaterra and R. Ruzicka, *Farben-Ztg.*, 1932, 37, 1547; *Brit. Chem. Abs. B*, 1932, 900.

<sup>217</sup> See S. Fokin, *J. Russ Phys.-Chem. Soc.*, 1907, 39, 609; 1908, 40, 276; *J.S.C.I.*, 1907, 26, 1149; *Chem. Abs.*, 1908, 2, 2896. W. M. Mackey and H. Ingie, *J.S.C.I.*, 1917, 36, 317. F. Wilborn, *Farben-Ztg.*, 1927, 33, 862; *Chem. Abs.*, 1928, 22, 3054. V. S. Kiselev and I. I. Golovitskiy, *J. Chem. Ind. (Moscow)*, 1930, 7, 1348; *Chem. Abs.*, 1931, 25, 5303. C. Kranz and V. Krach, *Chem. News*, 1928, 137, 257; *Chem. Abs.*, 1929, 23, 5599. C. Kranz and F. Fischmann, *Chem. News*, 1932, 144, 161; *Chem. Abs.*, 1932, 26, 2878. W. S. Chase, *Paint, Oil and Chem. Rev.*, 1932, 93 (13), 11; *Chem. Abs.*, 1932, 26, 3389. F. Wilborn and E. Baum, *Chem. Umschau Fette, Öle, Wachse Harze*, 1932, 39, 98; *Chem. Abs.*, 1932, 26, 4188. V. S. Kiselev and L. I. Norina, *J. Chem. Ind. (Moscow)*, 1933, (4), 22; *Chem. Abs.*, 1933, 27, 5558. K. Winkler, *Farben-Ztg.*, 1933, 38, 504, 534; *Chem. Abs.*, 1933, 27, 1771. F. Wilborn, F. Wachholtz, O. Walther and H. Ulrich, *Farben-Ztg.*, 1932, 37, 1120, 1156; *Chem. Abs.*, 1932, 26, 4188. Chung-Chun Wang, *Science (China)*, 1933, 17, 881; *Chem. Abs.*, 1933, 27, 5992. H. Wolff and G. Zaidler, *Farben-Ztg.*, 1934, 39, 897, 921, 945, 967, 993; *Chem. Abs.*, 1935, 29, 361.

<sup>218</sup> L. L. Steele, *Ind. Eng. Chem.*, 1924, 16, 957. See also Kai Ho, *Chem. Ind. (China)*, 1932, 7, 1; *Chem. Abs.*, 1933, 27, 3092.

<sup>219</sup> H. Brendel, *Farben-Ztg.*, 1924, 29, 790; *J.S.C.I.*, 1924, 43, 433B. With special reference to cobalt driers see E. Gebauer-Fuelnegg and G. Konopatsch, *Ind. Eng. Chem.*, 1931, 23, 163. J. Hyman and C. R. Wagner, *J.A.C.S.*, 1931, 53, 3019. *Amer. Ink Maker*, 1934, 12 (3), 13; *Brit. Chem. Abs. B*, 1934, 370.

<sup>220</sup> Z. Talanov, *Masloboino Zhir. Delo*, 1926, (10), 46; *Chem. Zentr.*, 1927, 2, 2236. A. Zinoviev, *Masloboino Zhir. Delo*, 1928, (9), 3; *Chem. Zentr.*, 1929, 1, 2834. C. Coffignier, *Farben-Ztg.*, 1928, 33, 1350. E. Stock, *ibid.*, 1929, 34, 2075. See also *Mon. Paint.*, 1930, 18, 189; *Am. Paint, Varnish Mfrs. Assoc. Abs.*, 1930, 187.

<sup>221</sup> G. H. Pickard, *Am. Paint, Varnish Mfrs. Assoc., Circ.*, 1931, 404, 542; *Chem. Abs.*, 1932, 26, 1140. H. Wolff, *Farben-Ztg.*, 1931, 36, 2200; *Brit. Chem. Abs. B*, 1931, 1061. E. Stock, *Seifensieder-Ztg.*, 1931, 58, 144. A. I. Kogan and N. I. Churdenko, *Farben-Ztg.*, 1932, 37, 1664; *Chem. Abs.*, 1932, 26, 5774. C. A. Klebsattel, *Paint, Varnish Prod. Mgr.*, 1933, 9 (11), 28; *Official Digest, Fed. Paint, Varnish Prod. Clubs*, 1934, 135, 112; *Chem. Abs.*, 1934, 28, 348, 3601. *Paint, Oil, Chem. Rev.*, 1932, 93 (14), 11, 22; *Chem. Abs.*, 1932, 26, 3122. C. A. Knauss, *Official Digest, Fed. Paint, Varnish Prod. Clubs*, 1934, 136, 158; *Chem. Abs.*, 1934, 28, 4612. V. S. Kiselev and L. I. Norina, *J. Chem. Ind. (Moscow)*, 1933, 10, 22; *Chem. Trade J.*, 1934, 94, 144; *J. Inst. Petr. Tech.*, 1934, 20, 259A.

<sup>222</sup> See T. Yamada, *J. Soc. Chem. Ind. Japan*, 1930, 33, 412B; *Brit. Chem. Abs. B*, 1931, 500. F. Pohl, *German P.*, 395,646, 1922, addn. to 352,356, to C. Jager G.m.b.H.; *J.S.C.I.*, 1925, 44, 17B. M. S. Potolovskii, *Russian P.*, 30, 1924; *Chem. Abs.*, 1933, 27, 3724. G. S. Petrov, *Russian P.*, 607, 1925; *Chem. Abs.*, 1933, 27, 5560. G. L. Stadnikov, G. S. Petrov and A. I. Danilovich, *Russian P.*, 532, 1925; *Chem. Abs.*, 1933, 27, 5560. M. M. Gurvich, *Russian P.*, 26,393, 1928; *Chem. Abs.*, 1932, 26, 6164.

<sup>223</sup> Naphthenates are discussed more completely in Chapter 10. For a detailed treatment of this subject see Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, 1934.

heavy metal is then added and the resulting precipitate is washed by decantation. The product is dehydrated by fusion. To assist the fusion, plasticizers (castor oil, tolyl phosphate, cyclohexanone, etc.) are added during or following precipitation.<sup>224</sup> In another method of preparation naphthenic acid is mixed at ordinary temperature with weak-acid salts of metals.<sup>225</sup> Naphthenates are formed also by adding metallic oxides to a solution of naphthenic acid in an organic solvent.<sup>226</sup>

Concentrated, homogeneous solutions of naphthenate driers are produced by dissolving the naphthenates in drying or semi-drying oils or in their fatty acids.<sup>227</sup> The fatty acids may be replaced wholly or partially by unsaturated aliphatic or aromatic acids or by substituted benzoic acids.<sup>228</sup> The solubility of naphthenates in organic solvents is improved by fusion with not more than 10 per cent of a solid, saturated fatty acid containing 16-20 carbon atoms.<sup>229</sup>

Other metallic salts suggested as driers include those of o-keto-aromatic acids,<sup>230</sup> those of keto acids prepared from acid anhydrides and petroleum hydrocarbons<sup>231</sup> and those of benzoic acid derivatives in which a nuclear hydrogen atom has been replaced by a hydrocarbon radical.<sup>232</sup> It is stated that improved driers are formed by using the heavy-metal salts of acids of the general formula  $R-O-C_nH_{2n}-COOH$  in which R is either an alkyl group of more than 3 carbon atoms, a hydro-aromatic group or an aralkyl group.<sup>233</sup>

In the opinion of Zinoviev,<sup>234</sup> an ideal drier should have little effect on the color of the oil used, should not form a sediment, should dry in 8-12 hours, should have low acidity and high metal content and should be durable on aging.<sup>235</sup> The most universal and rational drier, according to Zinoviev, is lead-manganese linoleate.<sup>236</sup> Attempts have been made to set a standard for drying power of metallic

<sup>224</sup> F. Pohl and B. Isenbeck, U. S. P. 1,974,507, Sept. 25, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 7561. British P. 335,863, 1930, and its addns. 367,666, 1931, and 380,360, 1932, *Brit. Chem. Abs. B*, 1931, 20; 1932, 592, 1115.

<sup>225</sup> R. M. Gerlach, U. S. P. 1,875,999, Sept. 6, 1932; *Chem. Abs.*, 1933, 27, 199.

<sup>226</sup> F. Meidert, U. S. P. 1,878,962, Sept. 20, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 434.

<sup>227</sup> F. Meidert and H. Schatz, U. S. P. 1,916,805, July 4, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4699. German P. 576,939, 1933; *Chem. Abs.*, 1934, 28, 351. British P. 339,865, 1930, and its addn. 339,922, 1930; *Brit. Chem. Abs. B*, 1931, 261.

<sup>228</sup> British P. 353,172, 1932, addn. to 339,865 and 339,922, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 78.

<sup>229</sup> F. Meidert, U. S. P. 1,976,182, Oct. 9, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 7561. British P. 397,276, 1932; *Brit. Chem. Abs. B*, 1933, 879.

<sup>230</sup> H. A. Bruson, U. S. P. 1,880,759, Oct. 4, 1932, 1,939,621 and 1,939,622, Dec. 12, 1933, to Röhm & Haas Co.; *Chem. Abs.*, 1933, 27, 1527; 1934, 28, 1556. U. S. P. 1,934,033, Nov. 7, 1933, to Resinous Prod. & Chem. Co.; *Chem. Abs.*, 1934, 28, 663. French P. 711,198, 1930; *Chem. Abs.*, 1932, 26, 1809. German P. 600,691, 1934; *Chem. Abs.*, 1934, 28, 7562. H. A. Bruson, J. D. Robinson and O. Stein, U. S. P. 1,962,478, June 12, 1934, to Resinous Products & Chem Co; *Chem. Abs.*, 1934, 28, 4922. British P. 363,394, 1930; *Brit. Chem. Abs. B*, 1932, 355.

<sup>231</sup> H. A. Bruson, U. S. P. 1,882,762, Oct. 18, 1932, and 1,894,460, Jan. 17, 1933, to Resinous Prod. & Chem. Co.; *Chem. Abs.*, 1933, 27, 835, 2458. British P. 365,038, 1930; *Brit. Chem. Abs. B*, 1932, 494. French P. 703,490, 1930; *Chem. Abs.*, 1931, 25, 4282.

<sup>232</sup> H. A. Bruson, U. S. P. 1,933,520 and 1,933,521, Oct. 31, 1933, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1934, 28, 662. British P. 365,084, 1930; *Brit. Chem. Abs. B*, 1932, 517. French P. 711,199, 1930; *Chem. Abs.*, 1932, 26, 1810. H. A. Bruson, J. D. Robinson and O. Stein, U. S. P. 1,930,449, Oct. 14, 1933, to Resinous Products & Chem Co.; *Chem. Abs.*, 1934, 28, 180. H. A. Bruson, U. S. P. 1,927,867, Sept. 26, 1933; *Chem. Abs.*, 1933, 27, 5995.

<sup>233</sup> H. A. Bruson and O. Stein, U. S. P. 1,969,709, Aug. 7, 1934, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1934, 28, 6327. See also H. A. Bruson, U. S. P. 1,920,160, July 25, 1933, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1933, 27, 4942. British P. 413,728, 1933; *Brit. Chem. Abs. B*, 1934, 848. British P. 414,121, 1934; *Chem. Abs.*, 1935, 29, 179. These driers are discussed by H. A. Bruson and O. Stein, *Ind. Eng. Chem.*, 1934, 26, 1268. See also H. W. Klever, German P. 368,740, 1917; *J.S.C.I.*, 1923, 42, 707A.

<sup>234</sup> A. Zinoviev, *Masloboino Zhiv. Delo*, 1929 (2), 39, (2), 51; *Chem. Abs.*, 1930, 24, 4407.

<sup>235</sup> Studies of the effects of driers on paint durability have been made by various investigators. See A. W. Van Heuwerkerth, *Am. Paint, Varnish Mfrs. Assoc., Circ.*, 1932, 407, 80; *Chem. Abs.*, 1932, 26, 2607. F. L. Chinery, *Paint, Oil, Chem. Rev.*, 1932, 94, (10), 78; *Chem. Abs.*, 1933, 27, 613. Reports of Philadelphia, California and Cincinnati-Dayton-Indianapolis Clubs, *Am. Paint, Varnish Mfrs. Assoc., Circ.*, 1933, 423, 1933, 445; *Chem. Abs.*, 1933, 27, 613, 614; 1934, 28, 348; *Brit. Chem. Abs. B*, 1933, 975, 977. J. T. Baldwin, *Am. Paint, Varnish Mfrs. Assoc., Circ.*, 1929, 356, 588; 1930, 370, 492; *Chem. Abs.*, 1930, 24, 519; 1931, 25, 220.

<sup>236</sup> Some of the many methods for producing driers include the following: Reaction of metallic oxides or salts with acids in volatile organic solvents (F. Meidert, German P. 596,878, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5262. British P. 353,783, 1930; *Brit. Chem. Abs. B*, 1931, 1018).

soaps. It has been shown that one standard, the "aridyne,"<sup>227</sup> cannot be used because of the effects of concentrations, atmospheric conditions and the nature of the oils used.<sup>228</sup> The adsorption of the driers by pigments in the paint also has some effect on the drying power.<sup>230</sup>

The solubility of driers in various solvents is of considerable interest. Evans<sup>240</sup> gave some data on the solubility of soaps in transformer oil which are listed as follows:

Nickel oleate	—readily soluble	Calcium oleate	—almost insoluble
Nickel stearate	—soluble, but solution solid at ordinary temperatures	Aluminum ricinoleate	—almost insoluble
Nickel linoleate	—very slightly soluble	Tin oleate	—soluble
Nickel butyrate	—insoluble	Zinc oleate	—soluble
Lead oleate	—soluble in hot oil but not in cold	Copper oleate	—soluble

The solubility of driers in oils or diluents is said to be improved by adding a small amount of a polyhydric alcohol or of a sugar.<sup>240a</sup> In order to stabilize solutions of driers, that is, to prevent sedimentation and gelatinization, as much as 10 per cent of solid saturated fatty acids or solid free carboxylic acids or derivatives are added.<sup>241</sup> Examples are stearic, palmitic and benzoic acids, mixed crotonic and arachidic acids and mixed hippuric and salicylic acids. A phenol (e.g.,  $\beta$ -naphthol) was used by Thomas<sup>242</sup> to inhibit crystallization of driers during the drying of films of coating materials in which the driers are used.<sup>243</sup>

The behavior of aluminum soaps in various solvents is of interest because of their extensive use as flattening-agents in varnishes.<sup>244</sup> A study of the action of

reaction in the presence of amines (H. Schatz, German P. 546,771, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3686; British P. 370,550, 1931, *Brit. Chem. Abs. B.*, 1932, 614; French P. 723,442, 1931; *Chem. Abs.*, 1932, 26, 4190); passing a mixture of oil and metallic oxides through a colloid mill and then heating (I. T. Osnos, Russian P. 48,948, 1929; *Chem. Abs.*, 1931, 25, 1109). Some miscellaneous driers include the soaps of wool fat (German P. 533,275, 1930, to Norddeutsche Wollkammerei and Kammgarnspinnerei; *Chem. Abs.*, 1932, 26, 610; British P. 400,797, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1934, 28); soaps of fatty acids derived from coconut oil (R. A. Dunham, U. S. P. 1,982,048, Nov. 27, 1934, to Union Oil Co. of Calif.; *Chem. Abs.*, 1935, 29, 626), the soaps of hydroxy-fatty acids (British P. 346,812, 1930, to Gebrüder Borchers A.-G.; *Brit. Chem. Abs. B.*, 1931, 685; German P. 555,715, 1929; *Chem. Abs.*, 1932, 26, 6164; French P. 688,306, 1930; *Chem. Abs.*, 1931, 25, 834), the soaps of acids obtained by oxidizing mineral waxes (F. Pohl, German P. 518,094, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2531; British P. 311,716, 1928; *Chem. Abs.*, 1930, 24, 979) and the heavy-metal salts of sulphonic acids from petroleum (H. E. Buc, U. S. P. 1,753,493, Nov. 12, 1929, to Standard Oil Development Co.; *Brit. Chem. Abs. B.*, 1930, 69; British P. 321,980, 1928, to Standard Oil Development Co.; *Brit. Chem. Abs. B.*, 1930, 110; S. L. Langedijk, U. S. P. 1,947,652, Feb. 20, 1934, to N. V. de Bataafsche Petroleum Maatschappij; *Brit. Chem. Abs. B.*, 1934, 1094; Dutch P. 28,002, 1932, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, 27, 1363). A drier for Japanese lac consists of potassium dichromate, glycerol and oxalic acid (K. Usawa, Japanese P. 101,341, 1933; *Chem. Abs.*, 1934, 28, 5263).

<sup>227</sup> The drying power equivalent to 0.064 oz. oil-soluble lead per gallon of drier. (C. F. Carrier, *Am. Paint J.*, 1930, 14, (33), 70f; 14 (52D), 25; *Chem. Abs.*, 1930, 24, 3660; 1931, 25, 221.)

<sup>228</sup> C. F. Carrier, *Am. Paint, Varnish Mfrs. Assoc., Circ.*, 1931, 404, 635; *Chem. Abs.*, 1932, 26, 1140. W. G. Armstrong, *ibid.*, 1933, 445, 498; *Chem. Abs.*, 1934, 28, 348. See also M. Weger, *Chem. Rev. Fett u. Harz-Ind.*, 1897, 5 (1), 1; *J.S.C.I.*, 1898, 17, 360.

<sup>229</sup> H. A. Gardner, *Am. Paint, Varnish, Mfrs. Assoc., Circ.*, 1931, 403, 396; *Chem. Abs.*, 1932, 26, 608. E. A. Evans, British P. 267,174, 1927, to C. C. Wakefield and Co., Ltd.; *Brit. Chem. Abs. B.*, 1927, 386. See also H. T. Vulte and H. W. Gibson, *J.A.C.S.*, 1902, 24, 215.

<sup>240a</sup> German P. 551,354, 1929, to Hermann Wulff A.-G.; *Chem. Abs.*, 1932, 26, 4487.

<sup>241</sup> British P. 364,863, 1931, and 397,276, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2050; 1934, 28, 917. French P. 738,905, 1932; *Chem. Abs.*, 1933, 27, 2050. See also F. Meidert, U. S. P. 1,895,200, Jan. 24, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2590.

<sup>242</sup> C. A. Thomas, U. S. P. 1,940,613, Dec. 19, 1933, to Davton Synthetic Chemicals, Inc.; *Chem. Abs.*, 1934, 28, 1556. Canadian P. 340,937, 1934; *Chem. Abs.*, 1934, 28, 4256. French P. 720,444, 1931; *Chem. Abs.*, 1932, 26, 3941.

<sup>243</sup> Some metallic soaps have in themselves the property of preventing crystallization in varnishes. For example, lithium and cadmium resinates and oleates prevent precipitation in varnishes containing rosin (German P. 448,297, 1925, to Chem. Fabrik. K. Albert G.m.b.H.; *Chem. Abs.*, 1929, 23, 1294). Soaps of titanium, zirconium and thorium are used to prevent settling of pigments (British P. 399,183, 1932, to Titanium Pigment Co., Inc.; *Brit. Chem. Abs. B.*, 1933, 1019. French P. 734,601, 1932; *Chem. Abs.*, 1933, 27, 1215). Aluminum stearate is used similarly (E. Perry, *Paint, Varnish Prod. Mgr.*, 1931, 6 (3), 5; *Chem. Abs.*, 1932, 26, 605). Titanium stearate has been found to be better than aluminum stearate in suspending pigments. See L. W. Ryan and W. W. Flechner, *Ind. Eng. Chem.*, 1934, 26, 909. See also British P. 357,179, 1930 (*Brit. Chem. Abs. B.*, 1931, 1084) and French P. 698,153, 1930 (*Chem. Abs.*, 1931, 25, 8159) to Patent Fuels & Color Corp.

<sup>244</sup> Although aluminum soaps are preferred, other materials are used to produce a flattening effect.

these soaps has been made by Markowicz.<sup>245</sup> In aliphatic hydrocarbons pastes are formed but in aromatic hydrocarbons and terpenes the soaps swell and form gels. Licata<sup>246</sup> found that for making matt-varnishes hydrocarbons are more effective dispersing agents for aluminum stearate than are esters, alcohols and ketones. Better flat finishes are made with the stearate. Another statement of interest is that aluminum stearate is not a definite compound<sup>247</sup> and consequently its properties may be varied to suit the use intended for it.<sup>248</sup>

Metallic soaps are used to a great extent to modify paints and lacquers. They are employed in nitrocellulose lacquers to improve resistance to ultraviolet light<sup>249</sup> and to give flat finishes<sup>250</sup> or crackle finishes.<sup>251</sup> Bruson<sup>252</sup> has added the metallic salts of organic ketonic acids ( $R-CO-R'-COOH$ ) to nitrocellulose lacquers to increase their hardness and adhesiveness. A lacquer which forms washable coatings on wall-paper is made by adding a metal stearate to a nitrocellulose solution.<sup>253</sup> A varnish, stated to be elastic enough to coat natural or artificial leather is prepared by mixing nitrocellulose with oxidized cottonseed oil and 50-150 per cent of zinc naphthenate.<sup>254</sup>

Metallic resinates and other soaps find use in coating compositions for metals,<sup>255</sup> priming paints for wood or other porous surfaces,<sup>256</sup> coatings for concrete<sup>257</sup> and in non-penetrating paints.<sup>257a</sup> Some resinates are used in decorating-paints for ceramic material.<sup>258</sup>

To some extent metallic soaps are used in waterproofing-compositions for

See F. Wilborn, *Farben-Ztg.*, 1928, 33, 2169; *Chem. Abs.*, 1929, 23, 1292. H. Deckert, *Farben-Ztg.*, 1930, 36, 453, 504; *Chem. Abs.*, 1931, 25, 1106. C. Hornemann, *Farbe u. Lack*, 1931, 496, 513; *Chem. Abs.*, 1932, 26, 859. E. Fonrobert, *Farben-Ztg.*, 1932, 37, 1084; *Brit. Chem. Abs.*, B, 1932, 562. L. Kern, *Farbe u. Lack*, 1933, 514; *Chem. Abs.*, 1934, 28, 349. H. Wolf and B. Rosen, *Farben-Ztg.*, 1933, 38, 704; *Brit. Chem. Abs.*, B, 1933, 399. P. H. Faucett, *Paint, Oil, Chem. Rev.*, 1934, 96 (3), 8; *Chem. Abs.*, 1934, 28, 2925.

<sup>245</sup> E. Markowicz, *Farben-Ztg.*, 1928, 34, 326, 414, 503; 1931, 36, 2050, 2086, 2122; *Brit. Chem. Abs.*, B, 1929, 101; 1931, 1017. See also H. Wolf and J. Rabinowicz, *ibid.*, 1932, 37, 1050; *Brit. Chem. Abs.*, B, 1932, 562; *Farbe u. Lack*, 1931, 36, 428; *Brit. Chem. Abs.*, B, 1931, 1061. W. Ostwald and R. Riedel, *Kolloid-Z.*, 1935, 70, 67; *Brit. Chem. Abs.*, B, 1935, 163.

<sup>246</sup> F. J. Licata, *Official Digest, Paint, Varnish Clubs*, 1933, 129, 256; 1934, 135, 106; *Chem. Abs.*, 1934, 28, 349, 3601.

<sup>247</sup> See J. W. McBain and W. L. McClatchie, *J. A. C. S.*, 1932, 54, 3266.

<sup>248</sup> F. J. Licata, *Official Digest, Paint, Varnish Clubs*, 1933, 125, 160; *Chem. Abs.*, 1933, 27, 4105.

<sup>249</sup> H. Bradshaw, U. S. P. 1,962,132, June 12, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 4904. British P. 390,518 and 391,168, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 3094. See also Swiss P. 134,370, 1927, to George Fey & Co.; *Chem. Abs.*, 1930, 24, 1754.

<sup>250</sup> G. H. Mutersbaugh, M. Zucker, H. D. Heiser and W. A. Shope, U. S. P. 1,856,653, May 3, 1932, to Glidden Co.; *Chem. Abs.*, 1932, 26, 3686.

<sup>251</sup> F. C. Hoffman, U. S. P. 1,846,869, Feb. 23, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 2608. L. Barenfeld, German P. 508,556, 1928; *Chem. Abs.*, 1931, 25, 834. L. Kern, *Farbe u. Lack*, 1933, 125; *Brit. Chem. Abs.*, B, 1933, 355. E. H. Bucy, U. S. P. 1,965,453, July 3, 1934, to Atlas Powder Co.; *Chem. Abs.*, 1934, 28, 5691.

<sup>252</sup> H. A. Bruson, U. S. P. 1,987,570, Jan. 8, 1935, to Resinous Products & Chemical Co.; *Chem. Abs.*, 1935, 29, 1668.

<sup>253</sup> E. F. Arnold, U. S. P. 1,848,686, Mar. 8, 1932, to E. I. du Pont de Nemours and Co.; *Chem. Abs.*, 1932, 26, 2866. British P. 394,974, 1931; *Brit. Chem. Abs.*, B, 1933, 800.

<sup>254</sup> K. I. Meltzer, *Ovulad, Tekhniki Kozhob. Proizvodstvo*, 1932, (8), 27; *Chem. Abs.*, 1934, 28, 7559.

<sup>255</sup> W. H. Buell, U. S. P. 1,472,239, Oct. 30, 1923, to Conversion Prod. Corp.; *Chem. Abs.*, 1924, 18, 450. H. Schladebach and H. Hahle, U. S. P. 1,844,983, Feb. 16, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2333. U. S. P. 1,983,006, Dec. 4, 1934; *Chem. Abs.*, 1935, 29, 625. German P. 570,738, 1933; *Chem. Abs.*, 1933, 27, 4427. British P. 305,218, 1929, and 323,525, 1928; *Brit. Chem. Abs.*, B, 1930, 204, 623. Swiss P. 139,824, 1929; *Chem. Zentr.*, 1930, 2, 3079. W. Bauer, British P. 252,364, 1925; *Chem. Abs.*, 1927, 21, 2290. K. Kuwahara, Japanese P. 41,761, 1922; *Chem. Abs.*, 1924, 18, 477. Swiss P. 142,167, 1929, to "Cirine-Werke" J. Lorenz & Co.; *Chem. Abs.*, 1931, 25, 2311. G. H. Burgman, U. S. P. 1,867,306, July 12, 1932; *Chem. Abs.*, 1932, 26, 4726. E. Asser, British P. 294,436, 1928; *Chem. Abs.*, 1929, 23, 2050.

<sup>256</sup> C. Tauber, British P. 275,610, 1927, to G. Leuchte Nachf.; *Brit. Chem. Abs.*, B, 1928, 719. German P. 541,916, 1926; *Chem. Abs.*, 1932, 26, 2608. H. Alles, German P. 502,353, 1927; *Chem. Abs.*, 1930, 24, 4944. P. Jaeger, German P. 547,337, 1926; *Chem. Abs.*, 1932, 26, 3685. J. Scheiber, German P. 533,276, 1928; *Chem. Abs.*, 1932, 26, 610. German P. 548,264, 1929, to Strahl and Walker, Chem. Fabr.; *Chem. Abs.*, 1932, 26, 3686. French P. 664,173, 1928, to Fabriken Temporin; *Chem. Abs.*, 1930, 24, 979. Y. Kawai and S. Mori, Japanese P. 101,216, 1933; *Chem. Abs.*, 1934, 28, 5261.

<sup>257</sup> W. Gurnik, German P. 510,871, 1929; *Chem. Abs.*, 1931, 25, 1055. P. Daumer, *Peint, pig. vernis*, 1931, 8, 1576; *Chem. Abs.*, 1932, 26, 321.

<sup>257a</sup> W. Krumbhaar, *Paint, Varnish Prod. Mgr.*, 1934, 10 (2), 5; *Chem. Abs.*, 1934, 28, 1877.

<sup>258</sup> K. Nakatuti, Japanese P. 90,288, 1931; *Chem. Abs.*, 1931, 25, 4375. A. Nakatsuchi, *J. Soc. Chem. Ind. Japan*, 1931, 34, 67B; *Chem. Abs.*, 1931, 25, 3142.

fabrics,<sup>200</sup> paper, metals, wood, cement and concrete.<sup>200</sup> The addition of ferric linoleate to an asphaltic composition for coating rubber is said to increase the durability and luster of the final surface.<sup>201</sup> The soaps of copper, mercury and lead<sup>202</sup> are employed in toxic coating compositions and repellants for protecting materials from the action of bacteria, fungous growths and insects.<sup>203</sup> Rosenblum<sup>201</sup> used metallic soaps to modify phenol-aldehyde resins. (See Chapter 20.) As an example phenol or cresol, zinc oleate or abietate, formaldehyde (40 per cent) and colophony are heated together under reflux. The product is dehydrated and then heated with glycerol at 260°C., effecting partial esterification and yielding a resin with high melting point.

Metallic soaps have found some use in the rubber industry, acting as vulcanization accelerators,<sup>204</sup> scorch retarders<sup>205</sup> and plasticizers.<sup>206</sup> When added to rubber solutions some metallic soaps lower the viscosity so that increased amounts

<sup>200</sup> E. Kind-scher, *Gummi-Ztg.*, 1930, 45, 333; *Chem. Abs.*, 1931, 25, 548. British P. 286,257, 1928, to J. P. Bemberg A-G; *Brit. Chem. Abs. B*, 1929, 514. O. E. Cushman and B. F. Farington, U. S. P. 1,821,932, Sept. 8, 1931, to Standard Oil Co. of California, *Chem. Abs.*, 1931, 25, 5998. C. M. E. Schroeder, U. S. P. 1,829,877, Nov. 3, 1931, *Chem. Abs.*, 1932, 26, 858. J. McGavack, U. S. P. 1,839,983, Jan. 5, 1932, to Naugatuck Chem. Co., *Chem. Abs.*, 1932, 26, 1475. S. J. Hayes, U. S. P. 1,917,937 and 1,917,938, July 11, 1933, to Ludlow Mfg. Associates; *Chem. Abs.*, 1933, 27, 4691, 4692. W. H. Adams, U. S. P. 1,948,464, Feb. 20, 1934, to Eastern Finishing Works; *Brit. Chem. Abs. B*, 1934, 1110. German P. 597,033, 1934, to Firma Theod. Rotta, *Chem. Abs.*, 1934, 28, 5255. M. M. Chihkin and M. N. Sussmann, *Izvest. Tekstil. Prom. Torgov.*, 1931, 10 (12), 73, *Chem. Abs.*, 1932, 26, 5425. Note also the use of these soaps in artificial fabrics. G. H. Ellis, British P. 323,501 and 323,785, 1928, to British Celanese, Ltd., *Brit. Chem. Abs. B*, 1930, 281, 321. H. Dreyfus, French P. 677,263, 1929; *Chem. Abs.*, 1930, 24, 3119. British P. 339,896 and 366,110, 1930, to British Celanese, Ltd., *Brit. Chem. Abs. B*, 1931, 341; 1932, 336. C. F. Ryley and G. A. Awcock, U. S. P. 1,807,755, June 2, 1931, to Celanese Corp. of America, *Chem. Abs.*, 1931, 25, 4414. French P. 731,712, 1932, to Alchem Kunststoffe Union N. V.; *Chem. Abs.*, 1933, 27, 842. German P. 597,194, 1934, to Chem. Fabr. Stockhausen & Co.; *Chem. Abs.*, 1934, 28, 5255. Use on brush bristles. W. K. Teller, U. S. P. 1,953,980, Oct. 4, 1934, to Western Bottle Mfg. Co., *Brit. Chem. Abs. B*, 1935, 96.

<sup>201</sup> C. N. Exley and H. A. Rimmer, British P. 211,972, 1922; *J. S. C. I.*, 1924, 43, 392B. C. J. J. Fox, British P. 289,122, 1927, *Brit. Chem. Abs. B*, 1928, 456. A. F. Owen, U. S. P. 1,658,953, Jan. 24, 1928, to Naugatuck Chem. Co., *Chem. Abs.*, 1928, 22, 1019. Canadian P. 266,291, 1926; *Chem. Abs.*, 1927, 21, 996. H. J. Braun, *Chem-Ztg.*, 1929, 53, 913. *Chem. Abs.*, 1930, 24, 1184. Carleton Ellis, U. S. P. 1,737,006, Nov. 26, 1929, to Ellis-Foster Co., *Chem. Abs.*, 1930, 24, 706. F. D. Snell, U. S. P. 1,792,661, Feb. 17, 1931; *Chem. Abs.*, 1931, 25, 2264. M. B. Chittick, U. S. P. 1,814,292, July 14, 1931, to Pure Oil Co., *Chem. Abs.*, 1931, 25, 5268. W. T. Dean, Canadian P. 308,096, 1931, to Calcel Prod. Co., British P. 375,002, 1931, to I. G. Farbenund A-G, *Brit. Chem. Abs. B*, 1932, 807. E. Sakuma and T. Wada, Japanese P. 93,055, 1931, *Chem. Abs.*, 1932, 26, 4486. J. C. Kiatoville, U. S. P. 1,858,830, May 17, 1932, to Barrett Co., *Chem. Abs.*, 1932, 26, 3897. British P. 380,776, 1932, to Felten & Guillaume Carlswek A-G, *Chem. Abs.*, 1933, 27, 5125. B. I. Ruback, Russian P. 33,242, 1933, *Chem. Abs.*, 1934, 28, 3377.

<sup>202</sup> A. M. Alvaado and A. N. Parrett, U. S. P. 1,955,355, Apr. 17, 1934, to E. I. du Pont de Nemours & Co., *Brit. Chem. Abs. B*, 1935, 161.

<sup>203</sup> The soaps of other metals are used to some extent for this purpose. See, for instance, S. W. Kendall (British P. 247,242, 1924, *Chem. Abs.*, 1927, 21, 656. Canadian P. 282,081, 1928, *Chem. Abs.*, 1928, 22, 3502) and R. Harvey and H. V. Day (U. S. P. 1,827,083 Oct. 13, 1931, to Pantasote Leather Co.; *Chem. Abs.*, 1932, 26, 606). Strontium oleate is used for moth-proofing. See British P. 365,233, 1930, to I. G. Farbenund A-G, *Brit. Chem. Abs. B*, 1932, 338.

<sup>204</sup> D. C. Paiman, E. W. Lauke, F. C. Bishop and R. C. Roark, U. S. Dept. Agr., *Tech. Bull.*, 1928, 80, 1-14; *Chem. Abs.*, 1929, 23, 1713. M. Lopez, *Quim. ind.*, 1929, 68, 222. *Chem. Abs.*, 1930, 24, 250. A. C. Robertson, *Ind. Eng. Chem.*, 1931, 23, 1093. J. Bux, *Quim. e ind.*, 1932, 9 (98), 53; *Chem. Abs.*, 1932, 26, 3077. H. F. Kalusowski, U. S. P. 1,481,012, Jan. 15, 1924, to J. Scharr & Co.; *Chem. Abs.*, 1924, 18, 878. R. M. Gerlach, British P. 277,083, 1928; *Chem. Abs.*, 1928, 22, 245. H. Schotte and K. Gornitz, German P. 538,188, 1928, to Schering-Kahlbaum A-G; *Chem. Abs.*, 1932, 26, 1703. E. Dal, Belgian P. 354,606, 1928; *Chem. Abs.*, 1929, 23, 3069. E. Meick, Swiss P. 108,018 and 118,144, 1925; *Brit. Chem. Abs. B*, 1928, 240. J. V. Evre and H. Langwell, British P. 367,913, 1930, to the Distillers Co. Ltd., *Brit. Chem. Abs. B*, 1932, 465. V. R. Abranis, U. S. P. 1,769,983, July 8, 1930, to A. N. Shlander, *Chem. Abs.*, 1930, 24, 4609. F. W. Sullivan, Jr. and E. W. Adams, U. S. P. 1,800,114, April 7, 1931, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1931, 25, 3119. J. L. Russell and H. E. Melton, U. S. P. 1,820,761, Aug. 25, 1931, to C. E. Jamieson and Co.; *Chem. Abs.*, 1931, 25, 5737. D. B. Bradner, Canadian P. 311,489, 1931, to the Canadian Industries, Ltd.; *Chem. Abs.*, 1931, 25, 3502. Y. Tubakimoto, Japanese P. 90,229, 1931, to Daichi Kogyo Seiyaku K. K.; *Chem. Abs.*, 1931, 25, 3119. D. B. Bradner, U. S. P. 1,843,010, Jan. 26, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 1809. R. G. Medcalf and G. W. Allan, Australian P. 10,808, 1933; *Chem. Abs.*, 1934, 28, 6960.

<sup>205</sup> I. Rosenblum, U. S. P. 1,808,716, June 2, 1931, and 1,809,570, June 9, 1931; *Chem. Abs.*, 1931, 25, 4422. French P. 704,116 and 705,091, 1930; *Chem. Abs.*, 1931, 25, 4726, 5305. Metallic soaps are used to modify organic acids of high molecular weight. See L. Auer and L. Susztek, French P. 694,339, 1930; *Chem. Abs.*, 1931, 25, 1839.

<sup>206</sup> H. A. Depew, *Ind. Eng. Chem.*, 1932, 24, 565. J. E. C. Bongrand and L. S. M. Lejeune, British P. 405,032, 1932; *Brit. Chem. Abs. B*, 1934, 400.

<sup>207</sup> H. R. Thies, *Ind. Eng. Chem.*, 1931, 23, 1357. E. R. Bridgwater, U. S. P. 1,822,561, Sept. 8, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 6018.

<sup>208</sup> F. Jacobs, *Rev. gen. caoutchouc*, 1931, 8 (72), 26 (73), 18; *Chem. Abs.*, 1932, 26, 333.

of rubber can be used in paints.<sup>268</sup> To prevent uncured rubber surfaces from adhering to each other they are dusted with an aluminum or magnesium soap.<sup>269</sup> An artificial gutta-percha is obtained by adding an aluminum salt to a mixture of latex and natural resins and waxes so that the product contains more than 15 parts of aluminum soap and more than 100 parts of resin-wax mixture for each 100 parts of rubber.<sup>270</sup>

In the manufacture of lubricants extensive use has been made of metallic soaps, particularly those of aluminum and lead.<sup>271</sup> The soaps are usually mixed with petroleum stock to form oils and greases.

Mixtures of dyestuffs with metallic soaps form insoluble lake pigments whose principal use is in printing inks.<sup>272</sup>

Some of the miscellaneous uses for metallic soaps include their incorporation in electrical insulating materials,<sup>273</sup> various plastic compositions,<sup>274</sup> ceramics,<sup>275</sup>

<sup>268</sup> H. P. Stevens and N. Heaton, *J. Oil, Colour Chem. Assoc.*, 1934, 17, 8; *Chem. Abs.*, 1934, 28, 1875. H. P. Stevens, J. G. Bearn and S. C. Stokes, *British P.* 407,038, 1934, to Rubber Growers Assoc., Inc.; *Chem. Abs.*, 1934, 28, 4922. K. Shimada, *J. Soc. Rubber Ind. Japan*, 1933, 6, 604; *Chem. Abs.*, 1934, 28, 1889. French P. 41,067, 1931, addn. to 693,890, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1524.

<sup>269</sup> P. A. Davis, U. S. P. 1,823,855, Sept. 15, 1931, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1932, 26, 337. *British P.* 346,489, 1929; *Chem. Abs.*, 1933, 27, 444.

<sup>270</sup> E. S. Ali-Cohen, U. S. P. 1,739,566, Dec. 17, 1929; *Chem. Abs.*, 1930, 24, 988. *British P.* 313,373, 1928; *Brit. Chem. Abs. B*, 1929, 652. German P. 537,034, 1928; *Chem. Abs.*, 1932, 26, 1157.

<sup>271</sup> H. S. Garlick, *Chem. Trade J.*, 1931, 88, 581, *Ind. Chemist*, 1931, 7, 249, *Chem. Abs.*, 1931, 25, 4696. M. Reswick, *Iron Age*, 1931, 128, 816; *Chem. Abs.*, 1931, 25, 5978. F. M. Simpson and C. C. Wilch, *Refiner and Natural Gasoline Mfr.*, 1931, 10 (3), 77; *Chem. Abs.*, 1931, 25, 2554. C. G. Williams, *Mech. Eng.*, 1932, 54, 128; *Chem. Abs.*, 1932, 26, 2320. H. H. Willock, S. J. Caplan and J. E. Babb, U. S. P. 1,625,969, Apr. 26, 1927, to Waverly Oil Works Co.; *Chem. Abs.*, 1927, 21, 2080. Canadian P. 264,851, 1926; *Chem. Abs.*, 1927, 21, 1007. C. B. de Hart, U. S. P. 1,709,311, Apr. 16, 1929; *Chem. Abs.*, 1929, 23, 2821. T. J. Craig, *British P.* 338,919, 1929, to P. Spence & Sons, Ltd., *Brit. Chem. Abs. B*, 1931, 807. *British P.* 347,574, 1929, to Panoleum Co.; *Chem. Abs.*, 1932, 26, 1771. E. N. Klemgard, U. S. P. 1,749,251, Mar. 4, 1930; *Chem. Abs.*, 1930, 24, 2286. F. L. Koethen, U. S. P. 1,758,446, May 13, 1930, to Acheson Graphite Co.; *Chem. Abs.*, 1930, 24, 3355. T. W. Doell and E. N. Klemgard, U. S. P. 1,781,167, Nov. 11, 1930, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1931, 25, 201. A. J. Ducamp, *British P.* 368,025, 1931; *Brit. Chem. Abs. B*, 1932, 459. *British P.* 371,643, 1931, to "Yacco" S. A. F.; *Brit. Chem. Abs. B*, 1932, 636. French P. 720,117, 1931; *Chem. Abs.*, 1932, 26, 3916. R. R. Rosenbaum, U. S. P. 1,860,622, May 31, 1932; *Chem. Abs.*, 1932, 26, 3916. H. T. Bennett, U. S. P. 1,820,295, Aug. 25, 1931; *Chem. Abs.*, 1931, 25, 5737. H. T. Bennett, L. G. Story and H. B. Beckley, U. S. P. 1,806,734 and 1,806,735, May 26, 1931; *Chem. Abs.*, 1931, 25, 4117. W. J. McGill, U. S. P. 1,837,279, Dec. 22, 1931, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1932, 26, 1434. S. H. Diggs and F. S. Campbell, U. S. P. 1,830,984, Nov. 10, 1931, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1932, 26, 840. S. H. Diggs, U. S. P. 1,869,800, Aug. 2, 1932, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1932, 26, 5413. A. Horwitz, U. S. P. 1,881,591, Oct. 11, 1932, and 1,882,664, Oct. 18, 1932; *Chem. Abs.*, 1933, 27, 595, 836. F. C. Gebhart, U. S. P. 1,902,635, Mar. 21, 1933, to United Oil Mfg. Co.; *Chem. Abs.*, 1933, 27, 3326. *British P.* 406,399, 1932; *Brit. Chem. Abs. B*, 1934, 369. French P. 743,820, 1933; *Chem. Abs.*, 1933, 27, 4072. T. W. Doell, U. S. P. 1,867,695, July 19, 1932, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1932, 26, 5201. D. A. Yonge, *British P.* 376,310, 1932, to Shell-Mex; *Chem. Abs.*, 1933, 27, 4072. G. L. Southard, U. S. P. 1,804,124, May 5, 1931; *Chem. Abs.*, 1931, 25, 3825. E. N. Klemgard, Canadian P. 316,148 and 316,393, 1931, to the Shell Oil Co.; *Chem. Abs.*, 1932, 26, 1770. W. M. Bowyer and G. H. Jacobs, U. S. P. 1,953,904, April 3, 1934, to Peters Cartridge Co.; *Chem. Abs.*, 1934, 28, 3906.

<sup>272</sup> J. H. Caughlan, *British P.* 265,787, 1926; *Chem. Abs.*, 1928, 22, 505. French P. 654,745, 1928, to British Dyest. Corp.; *Chem. Abs.*, 1929, 23, 3815. *British P.* 309,148, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 1033. E. R. Allen and A. Siegel, U. S. P. 1,772,300, Aug. 5, 1930, to Grasselli Chemical Co., Reissue 18,590, Sept. 6, 1932, to Krebs Pigment & Color Corp.; *Chem. Abs.*, 1930, 24, 4942; 1933, 27, 196. *British P.* 334,874, 1929 and 399,956, 1930, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1930, 1164; 1932, 778. A. Siegel, Canadian P. 816,507, 1931; E. R. Allen and A. Siegel, Canadian P. 322,053, 1932, both to E. I. du Pont de Nemours & Co., to Grasselli Chemical Co., to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 1809, 3685. K. Kawamura, Japanese P. 98,935, 1933; *Chem. Abs.*, 1933, 27, 5995.

<sup>273</sup> F. S. Roman, *Proc. Am. Soc. Testing Mat.*, 1926, (65), 8; *Chem. Abs.*, 1926, 20, 3089. German P. 487,115, 1926, to Siemens-Schuckertwerke G.m.b.H.; *Brit. Chem. Abs. B*, 1927, 452. J. E. G. Lahousse, U. S. P. 1,802,517, Apr. 28, 1931; *Chem. Abs.*, 1931, 25, 3746. *British P.* 275,958, 1926, and 294,931, 1927; *Chem. Abs.*, 1928, 22, 2421; 1929, 23, 1971. French P. 633,171, 1928; *Chem. Abs.*, 1928, 22, 3472. H. A. Tunstall, *British P.* 381,716, 1932, to W. T. Henley's Telegraph Works Co., Ltd.; *Chem. Abs.*, 1933, 27, 5561. F. M. Clark and R. A. Russett, U. S. P. 1,952,158, Mar. 27, 1934, to General Electric Co.; *Chem. Abs.*, 1934, 28, 3818. P. A. Gulkovskii and M. E. Kellerman, Russian P. 32,588, 1933; *Chem. Abs.*, 1934, 28, 3500.

<sup>274</sup> N. R. Levy, U. S. P. 1,487,957, Mar. 25, 1924; *Chem. Abs.*, 1924, 18, 1885. J. J. H. Sturmeij, *British P.* 276,395, 1926; *Chem. Abs.*, 1928, 22, 2446. H. S. Snell, U. S. P. 1,752,580, Apr. 1, 1930, to Western Electric Co.; *Chem. Abs.*, 1930, 24, 2559. D. S. Velkovskii, Russian P. 27,774 and 28,292, 1928; *Chem. Abs.*, 1931, 25, 845. P. I. Houssais, French P. 721,403, 1930; *Chem. Abs.*, 1932, 26, 4142. C. D. Cory, Canadian P. 318,381, 1931; *Chem. Abs.*, 1931, 25, 4682. R. L. Kramer, U. S. P. 1,845,156, Feb. 16, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 2316. D. F. Smith, E. J. Pieper and C. C. Vogt, U. S. P. 1,875,056, Aug. 23, 1932, to Armstrong Cork Co.; *Chem. Abs.*, 1932, 26, 6036. G. A. New, U. S. P. 1,946,914, Feb. 13, 1934, to National Gypsum Co.; *Chem. Abs.*, 1934, 28,

paving material,<sup>276</sup> adhesives,<sup>277</sup> pyrotechnics and explosives,<sup>278</sup> friction materials (brake linings, etc.),<sup>279</sup> soldering fluxes,<sup>280</sup> sealing compositions,<sup>281</sup> fabric-coating preparations,<sup>282</sup> stencil sheets,<sup>283</sup> gasoline anti-knock agents<sup>284</sup> and in the purification of oils.<sup>285</sup>

The sticking of resins to molds is prevented by using a dusting powder comprising a metallic soap<sup>286</sup> or even better, by incorporating the metallic soap (e.g., zinc stearate) in the molding composition.<sup>287</sup>

2496. French P. 763,164, 1934, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1934, 28, 5264. German P. 599,298, 1934, to International Bitumen Emulsions Corp.; *Chem. Abs.*, 1934, 28, 6003.

276 O. Parkert, *Sprechsaal*, 1928, 59, 25; *Chem. Abs.*, 1927, 21, 2770. J. Wolf, *ibid.*, 1928, 61, 883, 905; *Chem. Abs.*, 1929, 23, 4034. K. Friedrich and C. Friedrich, British P. 309,755, 1928; *Brit. Chem. Abs. B*, 1929, 520. W. Rath, German P. 582,312, 1933, to Porzellanfabrik Kahla; *Chem. Abs.*, 1933, 27, 5168.

277 British P. 355,430, 1930, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1932, 26, 4189. French P. 718,507, 1931; *Chem. Abs.*, 1932, 26, 3372. D. M. Hepburn, S. S. Sadler and E. F. Cayo, U. S. P. 1,846,107, Feb. 23, 1932, to Amiesite Asphalt Co. of America; *Chem. Abs.*, 1932, 26, 2569. British P. 309,634, 1927; *Brit. Chem. Abs. B*, 1929, 520.

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278 W. O. Snelling, U. S. P. 1,473,257, Nov. 6, 1923; *Chem. Abs.*, 1924, 18, 471. H. C. Pritham, U. S. P. 1,708,151, April 9, 1929; *Chem. Abs.*, 1929, 23, 2573. S. S. P. Meek, U. S. P. 1,708,186 and 1,708,187, April 9, 1929, and 1,756,255, April 29, 1930, *Chem. Abs.*, 1929, 23, 2573; 1930, 24, 3115.

279 S. P. Howe, U. S. P. 1,798,605, Mar. 31, 1931; *Chem. Abs.*, 1931, 25, 3137. J. W. Watson and C. S. Redfield, U. S. P. 1,845,858, Feb. 16, 1932, to John W. Watson Co.; *Chem. Abs.*, 1932, 26, 2289. R. F. Nowalk, U. S. P. 1,845,056 and 1,845,096, Feb. 16, 1932, to John W. Watson Co.; *Chem. Abs.*, 1932, 26, 2288.

280 F. E. Harris, U. S. P. 1,757,118, May 6, 1930; *Chem. Abs.*, 1930, 24, 3210.

281 S. L. Willis and W. H. Woodford, U. S. P. 1,701,868, Feb. 12, 1929, to Remington Arms Co.; *Chem. Abs.*, 1929, 23, 1507. W. R. Thurston, U. S. P. 1,916,289, July 4, 1933; *Chem. Abs.*, 1933, 27, 4641.

282 E. Hamblin, Jr., U. S. P. 1,570,740, Jan. 26, 1926; *Chem. Abs.*, 1926, 20, 907. British P. 390,628, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 6013. A. N. Parrett, U. S. P. 1,932,231, Nov. 27, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 529.

283 A. de Waele, U. S. P. 1,819,078, Aug. 18, 1931, to D. Gestetner, Ltd.; *Chem. Abs.*, 1931, 25, 5741.

284 R. J. J. Camell and P. Lepers, French P. 688,883, 1930; *Chem. Zentr.*, 1931, 1, 722.

285 G. Petroff, British P. 289,561, 1927; *Chem. Abs.*, 1929, 23, 697. British P. 235,861, 1924, to British Thomson-Houston Co.; *Chem. Abs.*, 1926, 20, 986. French P. 38,659 and 38,873, 1930, addns. to 553,883, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 1768, 1819. R. H. Gardner and H. G. Hodge, U. S. P. 1,740,584, Dec. 24, 1929, to Sinclair Refining Co.; *Chem. Abs.*, 1930, 24, 1210.

286 H. M. Weber, U. S. P. 1,558,440, Oct. 20, 1925, to Ellis-Foster Co.; *Chem. Abs.*, 1926, 20, 513.

287 T. S. Huxham, U. S. P. 1,571,447, Feb. 2, 1926, to Carleton Ellis; *Chem. Abs.*, 1926, 20, 997.

## Chapter 38

### Natural Resin Esters

#### ESTER GUM

In the previous chapter it was noted that common rosin must be neutralized in some manner to render it useful in varnishes. An important method of accomplishing this is to convert the rosin acids into esters. The ester formed by the combination of rosin with 10-15 per cent of glycerol is known commercially as ester gum and is used extensively in varnish manufacture. Ester gum has decided advantages over both raw and hardened rosin with regard to durability, moisture-resistance and freedom from livering with basic pigments.

Although glycerol is the most commonly used esterification agent other polyhydric alcohols and to some extent monohydric alcohols and phenols are used. The agent employed must be cheap enough for commercial use and at the same time must impart good color and hardness to the ester. In varnish and lacquer manufacture the requirements for ester gum are pale color, softening point of 82-86°C. and acid number of about 5-10. To obtain a good grade of ester gum the rosin used must be clear and must have a high melting point and high acid number.<sup>1</sup>

In the formation of ester gum from glycerol and rosin complete esterification should yield glyceryl triabietate, and experience has shown that this ester has the most desirable properties. In actual practice, however, complete esterification is difficult so that the ester gum obtained consists of glyceryl triabietate plus small amounts of the mono- and diabietates and, in addition, some decomposition products and the original unsaponifiable matter in the rosin. Considerable technique is required to obtain an ester gum of satisfactory quality.

Assuming that rosin consists entirely of abietic acid,  $C_{19}H_{30}COOH$ , the amount of glycerol required to form the triabietate would be slightly more than 10 per cent of the weight of rosin.<sup>2</sup> In practice, in order to ensure complete esterification 12-15 per cent of glycerol is employed. When excess glycerol is used it can be removed from the ester gum by vacuum distillation. The presence of free glycerol in the product lowers the moisture-resistance of varnishes in which the ester gum is used.<sup>3</sup>

The formation of rosin esters was first accomplished by Schaal.<sup>4</sup> Natural resin acids are heated with hydroxy compounds (monohydric and polyhydric alcohols)

<sup>1</sup> See S. Babcock, *Proc. Am. Soc. Testing Materials*, 1930, 30 (2), 795; *Chem. Abs.*, 1931, 25, 2310.

<sup>2</sup> The structure of abietic acid is given in Chapter 37.

<sup>3</sup> General reviews on the preparation of ester gums are given in the following articles: H. Brendel, *Farben-Ztg.*, 1925, 31, 578; *Chem. Abs.*, 1926, 20, 832. B. Scheifele, *Verf. kroniek*, 1934, 7, 63. H. Hadert, *Farben-Chem.*, 1934, 5, 409; *Brit. Chem. Abs. B*, 1935, 33. V. Williams, *Synthetic and Applied Finishes*, 1933, 4, 24. A. Naurov, *Peintures, pigments, vernis*, 1930, 7, 1214, 1262; *Chem. Abs.*, 1931, 25, 2863. A. C. Johnston, *Ind. Eng. Chem.*, 1929, 21, 688. A. Murray, *Chem. Met. Eng.*, 1921, 25, 473. Carleton Ellis and L. Rabinovitz, *Ind. Eng. Chem.*, 1916, 8, 406.

<sup>4</sup> E. Schaal, U. S. P. 335,485, Feb. 2, 1886; Reissue 10,823, March 29, 1887; 368,494, Aug. 16, 1887 and 501,446, July 11, 1893. *British P.* 12,807, 1884; 9027, 1886 and 2308, 1890; *J.S.C.I.*, 1886, 5, 523; 1890, 9, 631. *German P.* 32,083, 1884; 38,467, 1886 and 69,441, 1890; *Ber.*, 1885, 18, 674R; *Chem. Zentr.*, 1887, 424; 1893, 2, 783.



hols, phenols and carbohydrates) to form the esters.<sup>5</sup> Acids or acid salts capable of absorbing water are sometimes added. An essential feature is the removal of the water formed by esterification. If the process is carried out under pressure the water collects in the form of steam, and if the esterification is performed in a partial vacuum this suffices for the removal of water. A third method of water removal is to pass heated neutral gases through the reaction mixture.

In one example of ester formation rosin is heated to 350°C. *in vacuo* to remove volatile constituents. The hard residue is mixed with 10 per cent of its weight of anhydrous glycerol and heated at 250°C. under several atmospheres pressure. Steam which forms in the reaction is allowed to escape. When the esterification is complete the esters are vacuum distilled to separate soft and hard portions.

In the partial-vacuum method, rosin is heated in a retort to 180-210°C. and 10-11 per cent of its weight of glycerol is added in a thin stream with constant stirring.<sup>6</sup> A vacuum of about 100 mm. is maintained. When all the glycerol has been added the temperature is gradually raised to 280°C. and agitation is continued until esterification is complete.<sup>7</sup> The crude ester is made harder by removing volatile constituents either by vacuum distillation or by distillation in a stream of an indifferent gas.<sup>8</sup>

Experiments were conducted by Murray<sup>9</sup> to determine the best conditions of temperature and time for the formation of ester gum. When glycerol was added to molten rosin at 150°C. reaction began immediately, accompanied by foaming of the mixture due to the formation of water. Although the fused material was clear, drops removed and cooled showed a milky appearance. The acid number decreased rapidly, but continued heating at 150-250°C. for hours failed to neutralize a great portion of the rosin, irrespective of the amount of glycerol used. When the temperature was raised to 290°C. (the boiling point of glycerol), however, the esterification was completed rapidly, forming an almost neutral product possessing an acid number of less than 5 when carefully prepared.<sup>10</sup> Murray found it necessary to keep the mixture covered during the reaction in order to prevent excessive discoloration and to reduce loss of glycerol which is rapidly carried off by the water vapor. He did not recommend the use of a condenser since water vapor must be allowed to escape.<sup>11</sup> The ester obtained by Murray possessed a lower melting point than the original rosin and was slightly more tacky. The author has observed, however, that a well-esterified product, if entirely free from uncombined glycerol, is less tacky than raw rosin.

In further experiments Murray found that esterification of rosin with glycerol is completed in 15 minutes at 290°C. Using 12 parts of glycerol with 100 parts of rosin an ester with an acid number of 5-10 was obtained in that time. It was noted however that continued heating caused a gradual increase in acidity, attributed to the decomposition of the ester. This behavior is analogous to that of the glyceryl esters of fatty acids (e.g., linseed oil), which on prolonged heating

<sup>5</sup> An alternative method suggested by Schaal consists in heating metallic salts of the resin acids with halogen or sulphur compounds of phenols.

<sup>6</sup> The apparatus used by Schaal is shown in Figure 121.

<sup>7</sup> This is determined by the soda test. Esterification is complete if a test portion dissolved in benzene or ether does not give up any soluble portions when mixed with an aqueous solution of sodium carbonate.

<sup>8</sup> Similar methods are outlined by M. Bottler in "Harze und Harzindustrie," Verlagsbuchhandlung Dr. M. Jänecke, Hannover, 1907.

<sup>9</sup> A. Murray, *Chem. Met. Eng.*, 1921, 25, 475.

<sup>10</sup> The fact that the temperature must be raised to complete the esterification is attributed by W. F. Darke and E. Lewis (*J.S.C.I.*, 1928, 47, 1086) to a final condensation action.

<sup>11</sup> Nevertheless, the author has obtained good results with an air condenser of such length that the steam will escape but the glycerol for the most part will return to the reaction vessel.

yield free fatty acids. It is necessary, therefore, to determine when esterification is complete and discontinue heating at that time.

Ellis and Rabinovitz<sup>12</sup> investigated the effect of conditions on the formation of rosin esters. Partial esterification was brought about by bubbling various gases through a molten mixture of rosin and glycerol at 280-300°C. The gases used were hydrogen chloride, carbon dioxide, hydrogen, air and oxygen. A product having an acid value of about 7 per cent of the original value of the rosin was obtained by bubbling hydrogen chloride for two hours through a mixture of 50 parts of rosin and 5-8 parts of glycerol at 285°C. The resulting ester was of good color and contained no hydrochloric acid. A reduction in acidity of over 80 per cent resulted from passing carbon dioxide for 75 minutes through a rosin-glycerol mixture at 290°C. With the exception of hydrogen chloride, the action of the gases is largely mechanical, serving to bring the reactants into intimate contact and to remove water vapor. Non-oxidizing gases proved more satisfactory than hydrogen chloride or air since the air caused darkening and the hydrogen chloride showed a tendency to form a soft product.

The method of esterification was improved by using a stirring device so that the mechanical effect of the gases was obtained without the disadvantage of loss of glycerol. Another improvement was the use of a reflux condenser arranged to permit the escape of water vapor but to condense glycerol vapors and return them to the reaction vessel. Products obtained in this way had in some cases acid numbers as low as 6 or 7. A closed kettle equipped with a stirrer is best for the production of ester gum of good quality.

Improvements in the manufacture of ester gum have involved the use of various catalysts. Ellis and Weber<sup>13</sup> proposed to utilize basic substances capable of forming resinates. The resinates then react with glycerol to form a resinous complex. In one example 300 parts of rosin and 12 parts of quicklime are heated at 290°C. for 30 minutes. Then 40 parts of glycerol are stirred in and the mixture is agitated at 270-290°C. for another 30 minutes. The resulting product has an acid number of 9. Materials proposed in place of quicklime include calcium cyanamide, magnesia and barium oxide. In using this method Lafon<sup>14</sup> noticed that calcium resinate has a decided catalytic effect.<sup>15</sup> Kulas and Scheiber<sup>16</sup> obtained a non-sticky ester by mixing 3 parts of slaked lime with 100 parts of rosin and 5 parts of glycerol and working the mass on rolls heated to 250°C.

Sterling, Grothsch and Veitch<sup>17</sup> found that zinc and its salts are effective catalysts in preparing resin esters. When zinc metal is employed it is either introduced into the reaction mixture as a powder or the reaction container is lined with zinc. The catalyst speeds the reaction to four times its normal rate and only about 0.2 per cent of the zinc is taken up by the rosin. In one example 300 parts of rosin, 40 parts of glycerol and 1 part of finely divided zinc are heated together for 30 minutes at 275-280°C., using an air-cooled reflux condenser. The condenser is then removed and the temperature is raised to 310°C. to re-

<sup>12</sup> Carleton Ellis and L. Rabinovitz, *Ind. Eng. Chem.*, 1916, 8, 406. U. S. P. 1,226,760, May 27, 1917, to Ellis-Foster Co. and to Indestructible Paint Co., Ltd.; *Chem. Abs.*, 1917, 11, 2156.

<sup>13</sup> Carleton Ellis and H. M. Weber, U. S. P. 1,381,863, June 14, 1921 and 1,482,919, Feb. 5, 1924, to Ellis-Foster Co.; *Chem. Abs.*, 1921, 15, 3580; 1924, 18, 1058.

<sup>14</sup> P. F. Lafon, *Chimie et industrie*, 1925 (Sept. Special), 468; *Chem. Abs.*, 1926, 20, 512.

<sup>15</sup> The resinates of cadmium and lithium have been proposed. See German P. 448,297, 1925, to Chem. Fabr. Dr. K. Albert G.m.b.H.; *Brit. Chem. Abs.* B, 1928, 866.

<sup>16</sup> C. Kulas and J. Scheiber, German P. 436,770, 1924. British P. 230,861, 1925; *J.S.C.I.*, 1925, 44, 890B. French P. 594,932, 1925. Swiss P. 116,160, 1925; *Chem. Zentr.*, 1927, 1, 529.

<sup>17</sup> W. F. Sterling, V. E. Grottsch and F. P. Veitch, U. S. P. 1,395,874, Nov. 1, 1921, to the U. S. Gov't. and People; *Chem. Abs.*, 1922, 16, 653.

move excess glycerol. The product is said to have an acid number less than 1.5 and similar results are obtained using zinc oxide or zinc carbonate.<sup>18</sup>

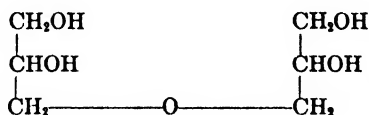
Investigations made by Beegle<sup>19</sup> showed that steel is an efficient catalyst for rosin-ester formation but that this metal has the disadvantage of giving a dark-colored product. Other catalysts tested were aluminum, copper, lead acetate and cobalt sulphate. An aluminum vessel was recommended for the esterification since it yields a clearer and paler product and has a greater catalytic effect than copper.<sup>20</sup> Kogan<sup>21</sup> found that in the preparation of glycerol esters of rosin by heating the components in a current of air at 275-280°C. the best catalyst is zinc. Sodium acetate, magnesium, aluminum and cadmium follow in decreasing effectiveness. Although zinc chloride, hydrogen chloride and ferric chloride are very efficient catalysts for the reaction they cause a certain amount of decomposition, yielding products which are half liquid and very sticky.

According to Voss<sup>22</sup> the formation of resin esters is greatly accelerated by the addition of a small amount of an oxygenated phosphorus compound (e.g., orthophosphoric or orthophosphorous acid). Other catalysts used by Voss in resin-ester formation are aliphatic hydroxy-carboxylic acids of low molecular weight.<sup>23</sup> In one example 300 parts of rosin are heated to 180°C. with 35 parts of glycerol and then 25 parts of diglycolic acid are introduced. The mixture is held at 280-285°C. for 1 hour in an atmosphere of carbon dioxide and for an additional 30 minutes in a vacuum at the same temperature. The product is said to be a pale, ash-free resin with an acid value of 22.

Drying oils, particularly tung oil, have a catalytic effect on esterification of rosin. This is dealt with later in the chapter.

Williamson and Beisler<sup>24</sup> suggested a process for making ester gum directly from crude turpentine. The mixture is strained and heated with 12.5 per cent of glycerol to 170°C. to drive off the water and part of the turpentine. The still is equipped with a reflux condenser adjusted to allow the escape of the water and turpentine but to retain the glycerol. A slow current of steam is passed through the mass until a temperature of 240°C. is reached. Then the steam is shut off and the temperature is increased to 290°C. where it is maintained for 1.5 hours to insure complete esterification of the rosin. Next, the reflux condenser is removed and for 10 to 15 minutes a rapid flow of steam is passed through the mixture, maintained at 275-290°C. to remove any excess of glycerol. This procedure is said to give light-colored products.

**Use of Other Polyhydric Alcohols.** If glycerol is heated with certain dehydrating agents, glycerol ethers or polyglycerols are formed. Thus two molecules of glycerol can condense to form diglycerol, one molecule of water being removed.<sup>25</sup>



<sup>18</sup> Tin has been proposed also. See E. H. Zollinger, British P. 183,897, 1921; *J.S.C.I.*, 1922, 41, 786A.

<sup>19</sup> F. M. Beegle, *Ind. Eng. Chem.*, 1924, 16, 953.

<sup>20</sup> See also K. Nakaya, *Bull. Kyoto Ind. Research Inst.* 1928, 3, 1-11; *Chem. Abs.*, 1930, 24, 1538.

<sup>21</sup> A. Kogan, *Masloboino Zhir., Delo*, 1930, 9-10, 32; *Chem. Abs.*, 1932, 26, 3940.

<sup>22</sup> A. Voss, German P. 561,158, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1219.

<sup>23</sup> A. Voss, German P. 577,691, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 663.

<sup>24</sup> B. F. Williamson and W. H. Beisler, U. S. P. 1,699,646, Jan. 22, 1929; *Chem. Abs.*, 1929, 23, 1293. U. S. P. 1,734,987, Nov. 12, 1929; *Chem. Abs.*, 1930, 24, 740.

<sup>25</sup> The condensation of glycerol to polyglycerol is catalyzed by a small proportion of iodine according to H. Hibbert (*J.A.C.S.*, 1915, 37, 1748. U. S. P. 1,126,407, Jan. 26, 1915; *Chem. Abs.*, 1915, 9, 694). For preparation of polyglycerols see R. Leopold and K. Billig, German P. 566,032, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 998. See also Chapter 42.

The use of polyglycerols to form rosin esters was advocated by Symmes<sup>20</sup> who found that such esters are harder and have a higher melting point than the usual ester gum. For the formation of polyglycerols Symmes used anhydrous sodium acetate or sodium hydroxide as a polymerization catalyst. As an illustration of the method employed, 200 parts of glycerol, 5 parts of zinc dust and 1 part of anhydrous sodium acetate are heated under reflux at 270-290°C. for 2 hours. Then 1000 parts of rosin are added and the mixture is heated at 290°C. for 15 hours. Unreacted constituents are removed by heating under reduced pressure. The resulting diglycerol ester has an acid number of 12. The method may be varied by separating the diglycerol from the other polyglycerols after the first step, and then reacting the diglycerol with rosin or pure abietic acid.

It has been stated that in addition to the harder product obtained by the use of polyglycerol there is also the advantage that the presence of an excess of polyglycerol in the ester has no harmful effect in lacquers whereas free glycerol in lacquers and varnishes lowers their moisture-resistance. Indeed some polyglycerols are reported to assist in the blending of ester gum with nitrocellulose.<sup>21</sup>

Similar to the use of glycerol is the employment of glycols to esterify rosin. Norman<sup>22</sup> obtained rosin esters of ethylene glycol and of diethylene glycol with the use of catalysts such as zinc dust or boric acid.<sup>23</sup> In one case 60 parts of diethylene glycol, 300 parts of rosin and 5 parts of catalyst are heated at atmospheric pressure for 5 hours at 250-260°C. under reflux and for 10 hours more without a condenser. Unreacted constituents are then removed by heating at 300°C. at about 15 mm. pressure. The result is 270 parts of ester with an acid number of 22 and a melting point of 60°C.

Esters of rosin with mono-esters and ethers of the glycols have also been prepared.<sup>20</sup> In one example 300 parts of rosin are heated with 152 parts of diethylene glycol monobutyl ether at 200-220°C. in an atmosphere of carbon dioxide. After 30-70 hours' heating the excess reagent is removed by blowing with carbon dioxide at 250°C. The product (yield 408 parts) has an acid number of 20-21.

In a similar manner polyhydric alcohols with more than 3 hydroxyl groups can be used to form rosin esters. Schmidt and Seydel<sup>24</sup> used sorbitol; and Bent and Johnston<sup>25</sup> employed pentaerythritol,  $C(CH_2OH)_4$ , erythritol,  $C_4H_8(OH)_4$ , and enneaheptitol,  $C_6H_{14}(OH)_7$ . Schaal<sup>26</sup> proposed the use of mannitol as well as carbohydrates. In experiments conducted by the author attempts to esterify rosin with carbohydrates yielded under ordinary conditions no satisfactory products. The rosin remained practically unchanged and the carbohydrates were converted into carbonaceous masses.<sup>21</sup>

The use of various halogen derivatives of polyhydric alcohols and ethers to

<sup>20</sup> E. M. Symmes, U. S. P. 1,696,337, Dec. 25, 1928, to Hercules Powder Co.; *Chem. Abs.*, 1929, 23, 848. See also V. V. Dmitrov, Russian P. 23,393, 1931 and 24,878, 1932, *Chem. Abs.*, 1932, 26, 1617, 1940, 4062.

<sup>21</sup> A. Fairbourn, G. P. Gibson and D. W. Stephens, *J. S. C. I.*, 1930, 49, 1069. See also Chapter 39.

<sup>22</sup> G. M. Norman, U. S. P. 1,779,710, Oct. 28, 1930 and 1,839,161, Dec. 29, 1931, to Hercules Powder Co.; *Chem. Abs.*, 1931, 25, 223; 1932, 26, 1297.

<sup>23</sup> I. I. Borgman (*J. Appl. Chem. Russia*, 1934, 7, 193, *Chem. Abs.*, 1934, 28, 7560) reported a 5 per cent yield of ester from heating rosin with 10 per cent of ethylene glycol at 180-235°C.

<sup>24</sup> German P. 509,368, 1928, to Chem. Fabr. Dr. K. Albert G. m. b. H.; *Chem. Abs.*, 1931, 25, 710.

<sup>25</sup> O. Schmidt and K. Seydel, German P. 500,504, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 4945.

<sup>26</sup> L. N. Bent and A. C. Johnston, U. S. P. 1,820,265, Aug. 25, 1931, to Hercules Powder Co.; *Chem. Abs.*, 1931, 25, 5780.

<sup>27</sup> E. Schaal, *loc. cit.*

<sup>28</sup> According to F. R. Suter (U. S. P. 905,384, Dec. 1, 1908, to New Process Varnish Co.; *Chem. Abs.*, 1909, 3, 959) dehydrated molasses will combine with rosin. The molasses is added to melted rosin and the product is mixed with an asphalt-distillate (primol) diluted with turpentine or alcohol to form a varnish.

produce resin esters has been proposed. For instance, Johnston<sup>37</sup> obtained glyceryl diabetate by the action of glycerol dichlorohydrin on sodium resinate. In the method used 75 parts of rosin are dissolved in a solution of 10 parts of sodium hydroxide in 100 parts of alcohol and the solution is refluxed at 80°C. Then 25 parts of glycerol dichlorohydrin are added gradually and the refluxing is continued for about 15 hours. The glyceryl diabetate formed is freed of sodium chloride by filtration, and of unreacted constituents by distillation. Other esters are formed similarly by using various chlorohydrins and bromohydrins, e.g., ethylene chlorohydrin or bromohydrin, propylene chlorohydrin and glycerol monobromohydrin.<sup>38</sup>

Langmeier<sup>37</sup> obtained glycol esters of abietic acid by the action of olefin dihalides on sodium resinate under pressures of 1-20 atmospheres and at temperatures of 75-200°C. In one case 45 parts of rosin are dissolved in 65 parts of an alcoholic solution containing 6 parts of sodium hydroxide. To this are added 10 parts of ethylene dichloride and the mixture is heated at 135-140°C. for 2 hours under 6-7 atmospheres pressure. The resulting ester has an acid number of 34.

Various aliphatic chloroethers were used by Humphrey<sup>38</sup> to form rosin esters. As an illustration a solution of 60 parts of sodium hydroxide and 500 parts of rosin in 700 parts of alcohol are heated with 110 parts of  $\beta,\beta'$ -dichloroethyl ether for 8 hours at 160°C. under a pressure of 15 atmospheres. Unreacted material is removed by distillation, leaving about 430 parts of diglycol diabetate. The product is softer than rosin and has an acid number of 5.

The esterification of colophony with alkylene oxides yields hydroxyalkyl esters of abietic acid, according to Schmidt and Meyer.<sup>39</sup> In one example, rosin is heated under pressure with ethylene oxide at 160-170°C. yielding a balsam-like resin. Similar treatment of ester gum was suggested. The resins are hardened in a vacuum or they may be acylated in the presence of a condensing agent, e.g., boric acid. The products can be used as softening agents with nitrocellulose lacquers.

**Esterification with Monohydric Alcohols.** The esters of rosin with aliphatic monohydric alcohols are for the most part viscous liquids some of which find use in lacquers particularly those made with nitrocellulose.<sup>40</sup>

A number of abietates of monohydric alcohols and phenols have been prepared and described by Kesler, Lowy and Faragher.<sup>41</sup> The alkyl esters were prepared by reaction of sodium abietate and the appropriate alkyl p-toluenesulphonate. The esters of the phenols were obtained by the action of phosgene on mixtures of dry sodium phenolates with sodium abietate. Special methods were used to form benzyl, cholesteryl and cetyl abietates. Some of the properties of the esters are recorded in Table 37.

In one of the various methods employed by Johnston<sup>42</sup> to produce alkyl

<sup>35</sup> A. C. Johnston, U. S. P. 1,771,044, July 22, 1930, to Hercules Powder Co., *Chem. Abs.*, 1930, 24, 4648.

<sup>36</sup> A. C. Johnston, U. S. P. 1,824,020, Sept. 22, 1931, to Hercules Powder Co., *Chem. Abs.*, 1932, 26, 324.

<sup>37</sup> A. Langmeier, U. S. P. 1,697,530, Jan. 1, 1929, to Hercules Powder Co., *Chem. Abs.*, 1929, 23, 1137.

<sup>38</sup> I. W. Humphrey, U. S. P. 1,843,284, Feb. 2, 1932, to Hercules Powder Co., *Chem. Abs.*, 1932, 26, 1812.

<sup>39</sup> O. Schmidt and E. Meyer, U. S. P. 1,845,198, Feb. 16, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2334. German P. 561,626, 1927; *Chem. Abs.*, 1933, 27, 1219. British P. 328,190, 1928; *Chem. Abs.*, 1930, 24, 5518. See also German P. 566,206, 1929, to Firma Louis Blumer, *Chem. Abs.*, 1933, 27, 1219.

<sup>40</sup> E. Schaal (German P. 32,083, 1885; *Ber.*, 1885, 18, 674R) suggested the use of methyl, ethyl, butyl, cetyl and ceryl alcohols to esterify rosin.

<sup>41</sup> C. C. Kesler, A. Lowy and W. F. Faragher, *J.A.C.S.*, 1927, 49, 2898. Ethyl abietate is described by A. C. Johnston, *Ind. Eng. Chem.*, 1929, 21, 688.

<sup>42</sup> A. C. Johnston, U. S. P. 1,682,280, Aug. 28, 1928 and 1,749,482, Mar. 4, 1930, to Hercules Powder Co.; *Chem. Abs.*, 1928, 22, 3892; 1930, 24, 2141. British P. 298,972, 1928; *Brit. Chem. Abs. B.*, 1930, 249. French P. 656,821, 1928; *Chem. Abs.*, 1929, 23, 4229.

TABLE 37.—Esters of Abietic Acid.

Ester	B.p. °C.	Press. mm.	M.p. °C.	Sp. gr. 15°/4°	Yield Per Cent
Methyl.....	225-226	16	—	1.050	—
Ethyl.....	204-207	4	—	1.032	85
n-Propyl.....	237-240	4	—	1.015	80
iso-Propyl.....	214-217	4	—	1.010	—
n-Butyl.....	247-250	3	—	1.014	95
iso-Butyl.....	222-225	4	—	1.008	80
iso-Amyl.....	254-257	4	—	1.001	72
Allyl.....	282-285	5	—	1.024	45
Phenyl.....	330-333	4	—	1.056	87
Hexalin.....	299-302	4	—	1.061	73
m-Tolyl.....	310-313	5	—	1.039	78
α-Naphthyl...	290 (decomp.)	2	—	1.116	78
Terpineol.....	310 (decomp.)	2	—	1.082	—
Benzyl.....	294-297	4	—	1.036	85
Cholesteryl...	—	—	122-125	—	94
Menthyl.....	—	—	77-83 (softens)	—	65
Bornyl.....	—	—	75-80 (softens)	—	75
Cetyl.....	—	—	42	—	—

esters of rosin an alkyl sulphate or halide is caused to react with rosin in alkaline solution. Alkyl sulphates are preferred to alkyl halides. As an example of the method used, 20 parts of sodium hydroxide are dissolved in 25 parts of water and 150 parts of ethyl alcohol. After the addition of 150 parts of rosin the mixture is heated under reflux until a clear solution results. Then 40 parts of diethyl sulphate are introduced into the solution and the alcohol is distilled off. The mixture remaining is heated and stirred for 1-2 hours at 145°C. The product, ethyl abietate, is removed by vacuum distillation and is obtained (in 80-85 per cent yield) as a clear ester with an acid number of about 10. An advantage of the method, according to Johnston, is that impure and dark-colored rosins can be employed because in the final distillation the color bodies do not distil over with the ester.

Johnston prepared alkyl rosin esters also by direct reaction between rosin and aliphatic alcohols. In one method a sulphonic acid is used as catalyst.<sup>43</sup> For example, to form ethyl abietate, 320 parts of rosin, 500 parts of ethyl alcohol and 10 parts of p-toluenesulphonic acid are heated for 4 hours at 160°C. under 11-12 atmospheres pressure. Excess alcohol is removed, the catalyst is neutralized with soda ash and the ethyl abietate (73 per cent yield) is obtained by distillation. Similar methods are employed for amyl and butyl abietates. By using higher temperatures (260-360°C.) and higher pressures (400-1700 pounds) and employing anhydrous alcohols esterification is effected without a catalyst.<sup>44</sup> Ethyl abietate was made by Gubelmann and Henke<sup>45</sup> by using as condensing agent either hydrochloric acid, sulphuric acid or oleum. For instance a mixture of 240 parts of 95 per cent ethyl alcohol, 80 parts of abietic acid and 36 parts of oleum (25 per cent) is refluxed until the abietic acid is 90 per cent esterified. The mass is diluted with water and the excess alcohol distilled off. Distinct layers of ethyl abietate and of sulphuric acid are found on standing. These are separated and the ethyl abietate is recovered by fractional vacuum distillation.

In a method devised by Butts,<sup>46</sup> ethyl abietate is produced by heating an ethyl

<sup>43</sup> A. C. Johnston, U. S. P. 1,840,395, Jan. 12, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1932, 26, 1812.

<sup>44</sup> A. C. Johnston, U. S. P. 1,924,934, Aug. 29, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 5338.

<sup>45</sup> I. Gubelmann and C. O. Henke, U. S. P. 1,829,481, Oct. 27, 1931, to Newport Co.; *Chem. Abs.*, 1932, 26, 737.

<sup>46</sup> D. C. Butts, U. S. P. 1,979,671, Nov. 6, 1934, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 367.

alcohol solution of abietic acid in a reaction chamber at 265°C. under a pressure of 800 pounds per square inch.

The reactions of high-molecular-weight alcohols with abietic acid have been studied in attempts to prepare resins with special properties. Stearyl alcohol and colophony were heated at 200°C. for a prolonged time by Fritz.<sup>47</sup> A liquid is obtained but upon standing it changes suddenly to a golden fatty mass having properties similar to those of rosin. A varnish resin can be made from ceryl, myricyl or other alcohols of the wax series and mineral or organic resins.<sup>48</sup>

Fonrobert and Greth<sup>49</sup> proposed changing abietic acid to abietic anhydride by treating colophony with acetic anhydride, and then esterifying with alcohols to give esters.

In the preparation of rosin esters, the chloride derivatives of monohydric alcohols are sometimes substituted for the alcohols. Previous mention has been made of a similar substitution in the case of polyhydric alcohols. The chloride derivatives often react more quickly with abietic acid than do the alcohols. Kränzlein and Voss<sup>50</sup> obtained a varnish resin by using 160 parts of rosin, 40 parts of benzyl chloride and 0.4 part of zinc chloride. The temperature was held at 100°C. until hydrogen chloride ceased to evolve and then maintained at 200°C. for one hour.

The catalysts suggested for esterifications with the organic chlorides are aluminum chloride, ferrous sulphate, cupric chloride, zinc resinate, tin, zinc and iron. Rosin has been used with the following organic chlorides; those of benzyl, benzal, tolyl, xylyl, methylbenzyl, dimethylbenzyl and isopropylbenzyl. All the esters prepared from these compounds were oil-soluble. To make them water-soluble, they are sulphonated.<sup>51</sup>

Another method of esterification calls for refluxing the sodium salt of abietic acid with an organic chloride. For instance, Crane<sup>52</sup> refluxed sodium abietate with benzyl chloride for 4 hours. The resulting ester was somewhat softer than rosin. Voss<sup>53</sup> used a solution consisting of alkali, rosin and ethyl chloride or chlorohydrin to prepare an oil-soluble resin.

A resin ester was made by Mossgraber<sup>54</sup> from sodium resinate and acetyl chloride. The product when mixed with  $\alpha$ -naphthylamine gave a resin for insulating-varnishes.

**Esterification of Rosin with Phenols and Naphthols.** The success that accompanied the esterification of rosin with alcohols led to investigations using other organic hydroxyl compounds. Among those first tried were phenol and naphthol.<sup>55</sup> The reactions between phenols or naphthols and rosin do not proceed as smoothly as those with glycerol.<sup>56</sup> The properties of the resins obtained from phenols and naphthols are such that the more easily prepared ester gum can frequently be used instead. In an attempt to get a more precise procedure

<sup>47</sup> F. Fritz, *Chem. Ztg.*, 1933, 57, 354; *Chem. Abs.*, 1934, 28, 2202

<sup>48</sup> E. C. Duhamel, French P. 673,310, 1928, to Comp. gén. des ind. textiles; *Chem. Abs.*, 1930, 24, 2623.

<sup>49</sup> E. Fonrobert and A. Greth, U. S. P. 1,948,573, Feb. 27, 1934, to Resinous Products and Chemical Co.; *Chem. Abs.*, 1934, 28, 2727.

<sup>50</sup> G. Kränzlein and A. Voss, U. S. P. 1,952,676, Mar. 27, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3605.

<sup>51</sup> British P. 361,951, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 357. British P. 314,588, 1929; *Brit. Chem. Abs. B*, 1929, 728. British P. 392,282. German P. 570,953, 1933; *Chem. Ztg.*, 1933, 57, (36), 76. K. Winter and N. Roh, German P. 555,083, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5221. See also G. Kränzlein and A. Voss, *loc. cit.*

<sup>52</sup> F. D. Crane, U. S. P. 1,513,802, Nov. 4, 1924; *J.S.C.I.*, 1925, 44, 16B.

<sup>53</sup> A. Voss, German P. 414,258, 1922, to Meister, Lucius & Brünning; *J.S.C.I.*, 1925, 44, 816B.

<sup>54</sup> E. Mossgraber, French P. 704,282, 1930; *Chem. Abs.*, 1931, 25, 4725. British P. 367,374, 1929; *Chem. Abs.*, 1933, 27, 2052.

<sup>55</sup> E. Schaal, German P. 32,083, 1885; *Ber.*, 1885, 18, 674R.

<sup>56</sup> In the author's laboratory, phenol, cresol, ethyl alcohol, aniline, and naphthylamine esterified by usual procedures did not give products approaching neutrality. Benzyl alcohol was the best compound tried.

for the esterification of rosin with phenol, Kogan, Makarenko and Sikar<sup>57</sup> made a study of conditions affecting these reactions. Phenol and rosin mixed in widely different proportions did not react when heated to 175°C. Partial esterification resulted from a 4-hour heating at 280°C. under 10 atmospheres pressure. Under these conditions a catalyst was necessary to complete the reaction. Zinc chloride, calcium oxide, sodium chloride, lead, iron, magnesium, and zinc were found effective. The phenol-rosin ester finally obtained was a soft sticky mass that would harden somewhat at 200°C. A varnish made from the hardened product was slow-drying and was inferior to ester gum in durability.

Some of the difficulties encountered in the esterification of rosin with phenol or cresol can be overcome by the use of proper catalysts. With boron trifluoride, a clear resin is produced and a lower temperature can be used. If the rosin and cresol are dissolved in carbon tetrachloride, the esterification occurs at room temperature.<sup>58</sup> Boric acid, which is also a catalyst for the manufacture of ester gum, has been suggested for the reaction between cyclohexanol and abietic acid. The cyclohexyl ester is a plasticizer for cellulose lacquers.<sup>59</sup> Aqueous mineral acids aid the combination of phenols with rosin. Resins made with help of these catalysts have melting points near 100°C.<sup>60</sup> A proposal by Pyhälä<sup>61</sup> calls for the preparation of rosin esters by the reaction of rosin with the calcium salts of the phenols at 180-220°C. The experimenter made esters of phenol, cresol, borneol,  $\beta$ -naphthol, resorcinol and glycerol from their calcium compounds. All the resins produced had a clear color. The low temperatures used probably help to bring about this result.<sup>62</sup>

Another variation in the procedure for esterifying rosin with phenols is to employ abietic anhydride in place of rosin.<sup>63</sup> Abietic acid is converted into abietic anhydride by treatment with acetic acid anhydride.<sup>63a</sup>

Resins to be employed in varnishes, lacquers and paints have been made by heating a mixture of tetrahydronaphthol and abietic acid.<sup>64</sup> Varnish resins were obtained by Binapff<sup>65</sup> by esterifying rosin incompletely with phenol and then completing the reaction with butyl or benzyl alcohol.

A water-soluble ester is prepared by condensing colophony with 1-naphthol-5-sulphonic acid.<sup>66</sup>

**Esterification of Rosin with Esters.** A variation in the preparation of rosin esters calls for heating abietic acid with a high-boiling ester to bring about an interchange of groups between the acid and ester. If the ester chosen has a high boiling point the required temperature can be maintained without pressure. The production of a neutral ester is facilitated if the resulting acid is volatile at

<sup>57</sup> A. J. Kogan, N. N. Makarenko and P. A. Sikar, *Farbe u. Lack*, 1934, 207, 218, 232; *Chem. Abs.*, 1934, 28, 4254.

<sup>58</sup> J. Binapff, German P. 582,846 and 582,847, 1933, and 605,688, 1934, additions to 581,956, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 919; 1935, 29, 1906. British P. 359,211, 1932; *Brit. Chem. Abs.* B, 1933, 1021. British P. 400,627, 1932; *Brit. Chem. Abs.* B, 1934, 29.

<sup>59</sup> British P. 390,534, 1933, to Deutsche Hydrierwerke A.-G.; *Chem. Abs.*, 1933, 27, 4939.

<sup>60</sup> A. Doser and A. Thauss, U. S. P. 1,788,371, Jan. 13, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1109. German P. 536,170, 1927; *Chem. Abs.*, 1932, 26, 1143. French P. 734,390, 1932; *Chem. Abs.*, 1933, 27, 1221.

<sup>61</sup> E. Pyhälä, *Farben.-Ztg.*, 1927, 33, 801; *Chem. Abs.*, 1928, 22, 3055. *Chem. Met. Eng.*, 1928, 16, 803. *Rev. prod. chim.*, 1928, 201. *Farben.-Ztg.*, 1928, 34, 816; *Chem. Abs.*, 1929, 23, 1292.

<sup>62</sup> For a critical review of the above work see A. I. Gelikh, *J. Chem. Ind. (Moscow)*, 1929, 6, 253; *Chem. Abs.*, 1929, 23, 3587; *Farben.-Ztg.*, 1928, 34, 1111.

<sup>63</sup> German P. 533,131, 1929, to Chem. Fabrik. K. Albert G.m.b.H.; *Chem. Abs.*, 1932, 26, 480. British P. 356,742, 1930; *Brit. Chem. Abs.* B, 1931, 1062. French P. 696,584, 1930; *Chem. Abs.*, 1931, 25, 2966.

<sup>63a</sup> The formation of abietic anhydride in this manner has already been noted above. (See ref. 49.)

<sup>64</sup> I. Gubelman and C. O. Henke, U. S. P. 1,829,480, Oct. 27, 1932, to Newport Co.; *Chem. Abs.*, 1932, 26, 861.

<sup>65</sup> J. Binapff, German P. 584,967, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1558.

<sup>66</sup> A. Thauss and H. Keppler, German P. 539,947, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2200.



the temperature of the reaction. Hesse,<sup>67</sup> in employing this method heated dimethyl and diethyl phthalate with colophony. In more recent work rosin has been heated with dibutyl phthalate, benzyl acetate, stearin and acetamide to give the corresponding butyl, benzyl, and glyceryl abietate and abietamide. To make butyl abietate, dibutyl phthalate and rosin (equal parts) were heated at 295-300°C for 8 hours. After the excess of abietic acid had been removed by benzene the butyl abietate had an acid number of 2.7.<sup>68</sup>

Aluminum has been employed as a catalyst in preparing esters by heating monoacetin, diacetin, glycol monoacetate or propylene glycol monoacetate with abietic acid.<sup>69</sup>

**Esterification of Rosin in the Presence of Drying Oils.** One of the advances in ester-gum manufacture was the addition of tung oil during the process of esterification. Tung oil acts as a catalyst for the reactions of glycerol with rosin. The resins produced are clear and make varnishes of good durability. The esters made have acid numbers of 7-21 and therefore may be used with basic pigments. The fume-loss during manufacture is less if tung oil is present. Gardner and Coleman<sup>70</sup> studied the esterification of rosin in the presence of tung oil in an open kettle. Tung oil up to 25 per cent of the rosin used improved the quality of the final resin. The addition of lime soap, (e.g., calcium resinate or tungate) accelerates the reactions of rosin and glycerol under these conditions. The temperature was maintained at 260°C during the process.

An illustration of the making of varnish utilizing these principles is given as follows:

*Waterproof Spar Varnish*

Rosin . . . . .	100 parts
Glycerol . . . . .	20 parts
Lime . . . . .	6 parts
Tung oil . . . . .	240 parts
Manganese tungate paste drier . . . . .	14 parts
Lead tungate paste drier . . . . .	8 parts
Turpentine . . . . .	66 parts
Mineral spirits . . . . .	300 parts

The method of incorporation is to melt the rosin with 25 parts of tung oil at 175°C. The lime is then added and thoroughly stirred into the mixture. At the same time the temperature is raised to 260°C. to dissolve the lime and bring about a partial polymerization of the tung oil. When the glycerol is added the temperature is lowered to 175°C. and then raised to 260°C. and held at that point for an hour. The mass is allowed to cool slightly when the remaining tung oil is added. Caution must be exercised in adding the oil to avoid a drop in temperature below 230°C. as the ester may be thrown out of solution and is redissolved with difficulty. The driers are added and the melt maintained at 230°C. to body the oil. This step may require from 30-60 minutes. A sample (pill) should be stiff but not gelatinous or stringy. When the requisite body is obtained the batch is cooled and thinners (turpentine first) added at 177-204°C. If the body of the varnish is heavy a larger proportion of thinners can be added. The turpentine may be replaced, at least to a very large extent, by mineral spirits. This varnish dried hard in 5 hours to give a flexible coating. A panel varnished with the composition showed no whitening or softening of the film after exposure to boiling water for 15 minutes. The acid value of the varnish was 5-6.<sup>71</sup>

<sup>67</sup> A. Hesse, U. S. P. 1,003,741, Sept. 19, 1911; *J.S.C.I.*, 1911, 30, 1223. German P. 227,667, 1909; *J.S.C.I.*, 1910, 29, 1394.

<sup>68</sup> British P. 353,616, 1929, to Chem. Fabrik. K. Albert G.m.b.H.; *Chem. Abs.*, 1932, 26, 5310. French P. 697,470, 1930; *Chem. Abs.*, 1931, 25, 3185. German P. 554,701, 1930; *Chem. Abs.*, 1932, 26, 6165.

<sup>69</sup> British P. 401,971, 1933, to British Celanese, Ltd.; *Chem. Abs.*, 1934, 28, 2923.

<sup>70</sup> H. A. Gardner and R. E. Coleman, *Crc., Paint Mfrs. Assoc.*, 1920, *Spec* 101; *Chem. Abs.*, 1920, 14, 2992. These workers gave the name "Tunga Resin" to their product.

<sup>71</sup> The circular by Gardner and Coleman contains directions for making both a short and a long oil varnish by this method. A short oil varnish is one containing 12 gallons or less of oil to 100 pounds of resin; one with 20 gallons or more is called a long oil varnish.

The esterification of rosin with glycerol in the presence of tung oil was further studied by Beegle.<sup>72</sup> He confirmed the fact that tung oil is an excellent catalyst for the formation of ester gums. Other substances that were found to be good catalysts include iron, cobalt, copper and aluminum. His results indicate that the use of tung oil in conjunction with an aluminum kettle would shorten the process by 30 minutes.<sup>73</sup>

Beegle concluded from his investigations that about 11 per cent of tung oil (based on rosin used) gave the clearest resins. The amount suggested was 1.5 gallons of tung oil to 100 pounds of rosin. Beegle also explored the possibility of esterifying rosin in the presence of a large proportion of tung oil to obtain a product that only needed thinning with turpentine when cooled. A mixture of 1160 grams of rosin, 160 grams of glycerol and 2268 grams of tung oil was heated to 270°C. The course of reaction was followed by determining acid numbers every 15 minutes. The acidity did not decrease as rapidly as expected, the indications being that too much oil was used.

The esterification of rosin in a congealed tung-oil-rosin varnish was proposed by Steinhoff<sup>74</sup> as a means of reclaiming the varnish. After the glycerol reacts with the rosin the varnish may be thinned as usual.

The esterification of rosin in the presence of acids derived from drying oils has been suggested as a means for the production of certain synthetic resins. Linoleic acid was used by Rosenblum.<sup>75</sup> His method proceeds as follows: 280 pounds of linoleic acid are heated to 250°C. with 100 pounds of glycerol until the acid disappears and thereupon 604 pounds of abietic acid are added. The mass is heated to 250°C. After cooling, an oil-soluble fusible resin is obtained. Linoleic acid was used with polyalcohols and colophony by Krzikalla and Wolff.<sup>76</sup> In these reactions a reduced pressure and moist atmosphere improve the quality of the final product.

Scheiber<sup>77</sup> substituted ricinoleic acid for linoleic. A mixture of ricinoleic acid and glycerol was heated and then rosin was added to neutralize excess glycerol. To aid the reaction between rosin and glycerol the whole was heated again. Oleic or polybasic organic acids can be mixed with resin acids before or after esterification with glycerol.<sup>78</sup>

Synthetic drying oils are said to be obtained by condensing castor oil with glycerol and esterifying the resultant product with a resin acid.<sup>79</sup>

**Reactions of Rosin with Drying Oils.** The reactions of rosin with drying oils have been investigated from two viewpoints; first, to determine if fatty oil glycerides of the oil react with rosin during the cooking of varnishes, and second, to find new methods by which resins and lacquers may be produced. A study was made by Pistor<sup>80</sup> to determine whether abietic acid and refined linseed oil or tristearin combine during the preparation of oil varnishes. In the experiment, abietic acid was mixed with the oil and after heating, the unesterified acid was removed by vacuum distillation. The proportion of acid left was found to depend upon time and temperature. The results obtained indicated only slight inter-

<sup>72</sup> F. M. Beegle, *Ind. Eng. Chem.*, 1924, 16, 953.

<sup>73</sup> F. M. Beegle, *Ind. Eng. Chem.*, 1924, 16, 1075.

<sup>74</sup> E. Steinhoff, *Paint, Oil, Chem. Rev.*, 1929, 87 (24), 21. *Oil and Fat Ind.*, 1929, 6 (10), 2543; *Brit. Chem. Abs. B*, 1929, 989.

<sup>75</sup> I. Rosenblum, U. S. P. 1,937,533, Dec. 5, 1933; *Chem. Abs.*, 1934, 28, 1208.

<sup>76</sup> H. Krzikalla and W. Wolff, German P. 529,483, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 8049. British P. 351,945, 1929; *Chem. Abs.*, 1932, 26, 3391.

<sup>77</sup> J. Scheiber, German P. 512,823 and 512,895, 1928; *Chem. Abs.*, 1931, 25, 1400. German P. 513,540, 1928; *Chem. Abs.*, 1931, 25, 2011. German P. 513,309, 1928. British P. 306,453, 1930; *Brit. Chem. Abs. B*, 1930, 871. British P. 358,933, 1930.

<sup>78</sup> German P. 580,282, 1933, to Firma Louis Blumer; *Chem. Abs.*, 1933, 27, 4943.

<sup>79</sup> K. Ott and B. Breyer, German P. 572,869, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3627.

<sup>80</sup> K. Pistor, *Farben.-Ztg.*, 1925, 30, 3056. *Farbe u. Lack*, 1925, 456; *Chem. Abs.*, 1926, 20, 117.

esterification between drying oils and rosin during the cooking of oil-rosin varnishes.

From experiments with rosin and linseed oil, Ragg<sup>81</sup> concluded that no glycerol-rosin ester is formed at the expense of the fatty acid glyceride. Upon heating rosin and linseed oil at 300°C. it was found that the free-fatty-acid content remains the same as that existing in the original fatty oil. Scheiber<sup>82</sup> believes that in the cases of rosin, Congo and Manila there is some displacement of the fatty acids of glycerides by resin acids during the cooking of varnishes. Wolff<sup>83</sup> thought that the heating of metallic resinates with linseed oil resulted in the formation of resin glycerides and metallic linoleates.

The reaction between rosin and oils has been suggested as a means of producing new resins. Bruson and Robinson<sup>84</sup> obtained a fusible product as a still-residue in the vacuum distillation of a mixture of castor oil and rosin. Bürstenbinder<sup>85</sup> utilized the action of tung oil with rosin to reliquefy coagulated tung oil.

Acids derived from drying and semi-drying oils may replace oils in the reactions with resin acids. The acids derived from tung, rapeseed and castor oil were condensed with rosin to produce lacquer substitutes.<sup>86</sup> Materials of a related nature proposed by Breyer<sup>87</sup> were made from hydroxyalkyl esters of drying oil acids and resin acids. A synthetic shellac was prepared by condensing the hydroxy acids from castor oil with oxidized rosin.<sup>88</sup>

Krzikalla and Wolff<sup>89</sup> used ricinoleic acid in conjunction with resinic acids. For example; 15 parts of ricinoleic acid were mixed with 13.5 parts of colophony and the mixture kept at 250°C. under reduced pressure for 10 hours, yielding a brown viscous oil, soluble in most organic solvents. Other substances that have been condensed with rosin include dihydroxyabietic acid, dihydroxystearic acid, salicylic acid, naphthenic acids, mesityl oxide and phorone.<sup>90</sup> Acids and alkalis are catalysts for the reactions of drying oil acids with resinic acids. If an inert atmosphere is used the resins produced are of better quality.<sup>91</sup>

**Chlorination of Rosin.** Chlorinated rosin is of interest because of its compatibility with cellulose acetate. Lacquers containing this resin give films of good flexibility and gloss. The addition of chlorine raises the softening point of rosin. The final resins are soluble in alcohol and benzene.

Rosenthal<sup>92</sup> chlorinated rosin by dissolving it in 10 times its weight of 19.5 per cent caustic soda solution and treating with a stream of chlorine gas. The precipitated resin was filtered and washed. The final product contained 5.5 per cent chlorine and had an acid number of 131.

Chlorine can be added to rosin under other conditions. Povlovski and Dmitrov<sup>93</sup> chlorinated rosin in the powdered form by heating it in an atmosphere of

<sup>81</sup> M. Ragg, *Farben.-Ztg.*, 1921, 26, 2335; *J. S. C. I.*, 1921, 40, 552A.

<sup>82</sup> J. Scheiber, *Farbe u. Lack*, 1929, 34, 393, 404, 418; *Chem. Abs.*, 1929, 23, 5336.

<sup>83</sup> W. Wolff, *Farben.-Ztg.*, 1926, 31, 1573; *Chem. Abs.*, 1926, 20, 2254.

<sup>84</sup> H. A. Bruson and J. D. Robinson, U. S. P. 1,889,348, Nov. 29, 1932, to Resinous Products & Chem. Co.; *Brit. Chem. Abs. B*, 1933, 1047.

<sup>85</sup> R. Bürstenbinder, *Chem. Umschau, Fette, Öle, Wachse, Harze*, 1931, 28, 229; *Chem. Abs.*, 1931, 25, 5582.

<sup>86</sup> G. Zilberman and A. Bolotin, *Lakokrasochnyye Ind.*, 1933, 2, 27; *Chem. Abs.*, 1933, 27, 4696.

<sup>87</sup> B. Breyer, German P. 542,087, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2333.

<sup>88</sup> J. Scheiber and W. Noack, U. S. P. 1,606,094, Feb. 21, 1928; *Chem. Abs.*, 1928, 22, 1486.

<sup>89</sup> H. Krzikalla and W. Wolff, U. S. P. 1,940,092, Dec. 19, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1558.

<sup>90</sup> G. M. Zilberman, Russian P. 29,215, 1931; *Chem. Abs.*, 1933, 27, 4110. See also French P. 569,517, 1923, to Konsortium für Elektrochem. Ind. G.m.b.H.; *Kunststoffe*, 1924, 14, 139. British P. 201,916, 1923; *Chem. Abs.*, 1924, 18, 178.

<sup>91</sup> British P. 339,958, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 213. French P. 697,700, 1930; *Chem. Abs.*, 1931, 25, 3160.

<sup>92</sup> L. Rosenthal, German P. 514,151, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1400.

<sup>93</sup> E. A. Povlovski and V. V. Dmitrov, Russian P. 8,907, 1929; *Chem. Zentr.*, 1931, 1, 1976.

chlorine. Lister<sup>94</sup> maintained melted rosin at 150-350°C. while treating with a halogen. Hypochlorous acid as well as chlorine will react with rosin.<sup>95</sup>

A chlorinated rosin containing 24.9 per cent chlorine and possessing a melting point of 100°C. was prepared by Dykstra.<sup>96</sup> He suggested that it be used as a soldering flux. Dux<sup>97</sup> obtained a shellac substitute by reacting chloroabietic acid with trihydroxystearic acid.

**Miscellaneous Reactions of Rosin.** From the foregoing it will be observed that the reagents proposed for combination with rosin are numerous and varied. Many of the products are of resinous nature but some of them differ so widely from the original rosin that they can hardly be called true resins.

Rosin treated with volatile inorganic halides gives resins having higher softening points, higher molecular weights and lower iodine numbers than the original substance. These resins are of interest because they are compatible with nitrocellulose. The halogenated product may be esterified with glycerol and alcohols by methods similar to those used for rosin. The resins are made by dissolving rosin in carbon tetrachloride, adding boron trifluoride and passing nitrogen through the solution. The reaction takes 33-35 hours at 10-11°C. Batavian dammar, gum mastic, copal and resin esters may replace rosin. The inorganic halides proposed in addition to boron trifluoride were the chlorides of titanium, aluminum and tin.<sup>98</sup>

Nitriles of abietic acid are made by treating abietic acid with gaseous ammonia. The nitriles are viscous balsams which are purified by distilling under reduced pressure. Dehydrating agents (e.g., aluminum oxide, thorium oxide, silica gel), are catalysts for the ammonia-rosin reaction. One method of preparation is given as follows: Gaseous ammonia and a benzene solution of rosin are heated to 350-360°C. in the presence of silica gel. The nitrile is separated from the benzene by distillation.<sup>99</sup>

The reaction of maleic anhydride or aconitic acid with rosin at 110°C. yields a resinous product with an iodine number of 63 (as compared with 180 for rosin) and a softening point of 100°C.<sup>100</sup> Acetylene was passed into rosin in the presence of mercuric acetate by Balle.<sup>101</sup> The resulting resin was soluble in lacquer solvents and fatty oils and possessed good drying qualities.

Some amine types of compounds have been suggested as reactants with rosin. A product made from trihydroxyethylamine and rosin is said to have good resistance to alkalis.<sup>102</sup> An example of the proportions used follows: A mixture of 37 parts of trihydroxyethylamine and 213 parts of rosin is heated in such a manner that a temperature of 300°C. is reached in 2-4 hours. The product melts at 75°C. and is soluble in benzol, ethyl acetate and drying oils.

Glycerylamine neutralized with abietic acid yields a hard resin that is soluble

<sup>94</sup> D. A. Lister, U. S. P. 1,957,788, May 8, 1934, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 4256

<sup>95</sup> E. Baum and W. O. Hermann, German P. 426,283, 1922, to Konsortium für Elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs.* B, 1926, 597.

<sup>96</sup> H. B. Dykstra, U. S. P. 1,785,115, Dec. 16, 1930, to Grasselli Chemical Co.; *Chem. Abs.*, 1931, 25, 484.

<sup>97</sup> W. Dux, British P. 300,956, 1927; *Brit. Chem. Abs.* B, 1930, 26.

<sup>98</sup> J. Binapf, German P. 564,867, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1219. German P. 575,122, 1933; *Chem. Abs.*, 1933, 27, 5996. British P. 399,206, 1933; *Chem. Abs.*, 1934, 28, 1881. French P. 734,390, 1932; *Chem. Abs.*, 1933, 27, 1221. French P. 735,918, 1932; *Chem. Abs.*, 1933, 27, 2053. French P. 760,126, 1934; *Chem. Abs.*, 1934, 28, 3606.

<sup>99</sup> O. Nicodemus and O. Wulff, German P. 580,281, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4816. British P. 390,120, 1933; *Chem. Abs.*, 1933, 27, 4544. French P. 749,970, 1933; *Chem. Abs.*, 1934, 28, 492.

<sup>100</sup> British P. 355,281, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 72. French P. 711,394, 1933. For a fuller description of reactions between rosin and maleic anhydride see Chapter 40.

<sup>101</sup> G. Balle, German P. 463,843, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 4262.

<sup>102</sup> K. Ott and F. Frick, German P. 578,870, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 918. See also *J.S.C.I.*, 1934, 53, 1030.

in benzene and can be added to lacquers.<sup>101</sup> Aromatic amines, e.g., aniline, react with colophony to give a product that may be condensed with furfural.<sup>101</sup>

Binapfl<sup>102</sup> raised the softening point of rosin by treatment with a carbazole. For instance rosin and diisopropylcarbazole were dissolved in benzene and held at 18°C. in the presence of boron trifluoride to give a product softening at 126°C.

Among other compounds, organic sulphonic acids have been proposed as alkylating agents for abietic acid. Voss<sup>103</sup> suggested that colophony, after treatment with sodium hydroxide, be alkylated with methyl-p-toluenesulphonate. After the removal of sodium p-toluenesulphonate by washing, the residue yielded a yellow viscous mass that behaved like Venice turpentine. Vulcanizable resins were produced by Auer<sup>104</sup> from colophony and  $\beta$ -naphthol-3,6,8-trisulphonic acid, dichlorobenzenesulphonic acid, sulphasalicylic acid or p-toluenesulphonyl chloride. The mixtures were heated for several hours at 300°C. under a vacuum to obtain the resin. Products with entirely different properties were prepared by heating abietic acid with sodium 3-chloro-2-hydroxypropanesulphonate or sodium bromoethanesulphonate. The temperature was held at 110-140°C. for 4-15 hours. Water containing small percentages of these reaction products may be used for cleaning textile fibers.<sup>105</sup>

Rosin was utilized by Pungs<sup>106</sup> to modify the properties of lignite wax. A mixture of 50 parts of wax and 20 parts of rosin was heated with air bubbling through for 3 hours at 160-170°C. The final wax melted at 80°C. and had an acid number of 42. A modification of this procedure calls for esterifying the rosin and wax composition with glycerol.<sup>107</sup>

Many substances have been added to rosin and glycerol preceding esterification in order to effect slight changes in the properties of the final product. Willard<sup>111</sup> used rosin, glycerol and rubber with a ferric oxide catalyst. Varnishes made from the resulting resin gave elastic films. Colophony, glycerol and polycarboxylic ketones were heated by Bruson<sup>112</sup> to obtain clear resins with high softening points. A rosin-aldehyde condensation product when treated with glycerol gives an oil-soluble resin.<sup>113</sup> A mixture of abietic acid and dihydroxydiphenylmethane dicarboxylic acids reacts with glycerol to give a product usable in nitrocellulose lacquers.<sup>114</sup>

**Crystalline Esters.** In a study of rosin esters, Wolff<sup>115</sup> found that a solution of ester gum in amyl acetate slowly deposited a crystalline precipitate. After three months the crystals were collected and proved to be glyceryl triabietate having a zero acid value, a saponification number of 54.4, a melting point of 172°C. and an average molecular weight of 955. Further supplies of the crystals were easily obtained by dissolving ester gum in warm ethyl acetate, adding a few drops

<sup>101</sup> A. Fairbourne, G. F. Gibson and D. W. Stephens, *J. S. C. I.*, 1930, **49**, 1069; *Chem. Abs.*, 1931, **25**, 1217.

<sup>102</sup> O. A. Cherry and F. Kurath, U. S. P. 1,894,580, Jan. 17, 1933, to Economy Fuse & Mfg. Co.; *Brit. Chem. Abs.*, **B**, 1933, 929.

<sup>103</sup> J. Binapfl, German P. 578,039, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, **28**, 4430.

<sup>104</sup> A. Voss, German P. 414,258, 1922, to Meister, Lucius & Bruning, *J. S. C. I.*, 1922, **41**, 816B.

<sup>105</sup> L. Auer, U. S. P. 1,980,367, Nov. 13, 1934, to J. R. Newman; *Chem. Abs.*, 1935, **29**, 366.

<sup>106</sup> H. J. Wieland, C. O. Henke and G. Etzel, U. S. P. 1,984,713, Dec. 18, 1934; *Chem. Abs.*, 1935, **29**, 858. H. J. Wieland, C. O. Henke and M. A. Prael, U. S. P. 1,984,714, Dec. 18, 1934; *Chem. Abs.*, 1935, **29**, 857, both patents to E. I. du Pont de Nemours & Co.

<sup>107</sup> W. Pungs, U. S. P. 1,780,632, Nov. 4, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, **26**, 4195.

<sup>108</sup> W. Pungs and K. Behringer, German P. 550,324, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, **26**, 4195.

<sup>111</sup> C. F. Willard, U. S. P. 1,587,622, June 8, 1926; *Brit. Chem. Abs.*, **B**, 1926, 680.

<sup>112</sup> H. A. Bruson, U. S. P. 1,829,038, Oct. 27, 1931, to Rohm & Haas Co.; *Brit. Chem. Abs.*, **B**, 1933, 238.

<sup>113</sup> G. M. Zilberman, A. A. Bolotin and P. M. Romanova, Russian P. 30,366, 1933; *Chem. Abs.*, 1933, **27**, 5562.

<sup>114</sup> O. A. Cherry, U. S. P. 1,982,788, Dec. 4, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, **29**, 523.

<sup>115</sup> H. Wolff, *Farben-Ztg.*, 1926, **31**, 1573; *Chem. Abs.*, 1926, **20**, 2254.

of benzene, cooling to 0°C. and seeding. By this procedure, a crop of crystals could be recovered in 3 days. As Wolff also obtained glyceryl triabietate on cooking metallic resinates with drying oils, he postulated as the varnish reaction that Glyceryl linoleate + Lead resinate  $\longrightarrow$  Glyceryl abietate + Lead linoleate.

An identical crystalline ester was obtained by Fonrobert and Pallauf<sup>116</sup> in a yield exceeding 10 per cent from a 50 per cent by weight solution of a pure rosin ester gum in hot acetone. Using samples of French, Spanish, American and German rosin and an English ester gum yields of 3 to 7 per cent were obtained. These crystals were found to be insoluble in ethyl alcohol (contrasting with glyceryl monoabietate and diabietate which are alcohol-soluble).

Crystals of glyceryl triabietate were prepared by Maly<sup>117</sup> by esterifying an alcoholic solution of abietic acid with glycerol. The crystals had a melting point of 125°C. and were soluble in alcohol and ether.

Nauroy<sup>118</sup> obtained crystals which were identified as 2-chloroglycerol diabietate. He dissolved abietic acid in a solvent consisting of equal parts of alcohol and xylene. After neutralizing with 0.5 *N* potassium hydroxide, the solution was refluxed 6 hours with a small proportion of trichlorohydrin. The precipitated potassium chloride was filtered off and the solution treated with carbon dioxide. The solvent was evaporated and the product crystallized from alcohol. The crystals had a melting point of 181°C., an acid value of 2.7 and a saponification value of 246.

#### MODIFICATION OF ESTERS

**Oxidation.** The addition of oxygen to ester gum has been proposed to modify its properties. Oxidation of ester gum raises its softening point and increases its solubility in many organic solvents. The temperature of ester gum during the reaction has to be controlled to avoid darkening the product. Schaal<sup>119</sup> used air to harden ester gum. Before treatment the rosin ester was powdered, mixed with a dehydrating agent (e.g., anhydrous sodium sulphate) and a catalyst (e.g., cobalt acetate or manganese borate). The whole mass was heated gradually to 100°C. and air passed through. After oxidation the inorganic substances were removed by water. The resulting material was directly soluble in oil.

Bradley<sup>120</sup> passed air over a thin layer of resin ester maintained at 60°C. After 4 days the softening point was raised from 90° to 121°C. The treatment increased the solubility of the ester gum in glycol mono esters and ethers. Slansky and Götz<sup>121</sup> reported that the properties of ester gum are improved by passing gases through the material while it is subjected to a silent electrical discharge.

Ozone has been used to hasten the drying of films produced from ester gum varnishes. Spence and Cochran<sup>122</sup> found that stoving a film in contact with ozone had no harmful consequences if ozone was absent during the first 10 minutes of the operation.

On long storage, surface oxidation of ester gum is great enough to change the color of varnishes made from it. For this reason ester gum stored in steel drums where it is one solid lump is better than that stored in wooden containers where

<sup>116</sup> E. Fonrobert and F. Pallauf, *Farben.-Ztg.*, 1926, 31, 1848; *Brit. Chem. Abs.* B, 1926, 594.

<sup>117</sup> R. Maly, *Z. für Chem.*, 1866, 33; Beilstein, "Handbuch. der Org. Chem.," L. Voss, Leipzig, 3rd. Ed., 1893, 2, 1436.

<sup>118</sup> A. Nauroy, *Peintures, pigments, vernis*, 1930, 7, 1214, 1262; *Chem. Abs.*, 1931, 25, 2863.

<sup>119</sup> E. Schaal, U. S. P. 1,583,014, May 4, 1926; *Brit. Chem. Abs.* B, 1926, 502. *British P.* 243,556, 1925; *Chem. Abs.*, 1926, 20, 3826. *German P.* 419,673, 1924; *Kunststoffe*, 1926, 16, 178.

<sup>120</sup> T. F. Bradley, U. S. P. 1,893,982, Jan. 10, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 2319.

<sup>121</sup> P. Slansky and W. Götz, *Farben.-Ztg.*, 1932, 37, 1419; *Brit. Chem. Abs.* B, 1932, 850.

<sup>122</sup> L. U. Spence and P. B. Cochran, *Trans. Amer. Electrochem. Soc.*, 1926, 50, 401; *Brit. Chem. Abs.* B, 1926, 178.

it is broken into small lumps because in the former case less surface is exposed to air.<sup>120</sup>

**Hydrogenation.** The resins resulting from the hydrogenation of rosin ester give films that are less brittle than those made from ester gum. As a consequence they are recommended for use in nitrocellulose lacquers. Basic pigments can be employed in conjunction with the hydrogenated esters.

It has been found that the reaction between esters and hydrogen is best carried out by having the esters in solution. The solvents suggested have been ethyl alcohol, butyl alcohol, benzene, toluene, ethyl acetate, petroleum naphtha and gasoline. To the solution there is added an activating acid (e.g., hydrochloric, phosphoric, acetic, formic). In addition to the acid, catalysts are used. The catalysts named have been nickel, palladium, platinum and chromites of copper, zinc and nickel. Under these conditions ethyl and methyl abietate have to be hydrogenated 4-5 hours to obtain a satisfactory product. To shorten the time still further the pressure must be greater than atmospheric. Pressures up to 2000 pounds per square inch have been suggested.

A procedure reported for the hydrogenation of the esters is as follows: 50 parts of ethyl abietate are dissolved in 148 parts of ethyl alcohol into which 2 parts of phosphoric acid have been put, 1 part of platinum oxide is incorporated and the solution is agitated under a pressure of 2 atmospheres at 25°C for 25 hours. By this treatment ethyl abietate takes up 70 per cent of the theoretical amount of hydrogen.<sup>124</sup>

It is possible to hydrogenate abietic acid before instead of after esterification. The properties of resins prepared by either method are similar.<sup>125</sup>

#### COPAL ESTERS

**Esterification of Copals with Glycerol.** Congo, Manila and Pontianac copals have the disadvantages which are inherent with resins possessing high acid number. For instance, varnishes made from them are likely to liver or stiffen if used with basic pigments to prepare enamels. The acid number of the copals is reduced by esterification in essentially the same manner as for rosin. Fossil resins esterified with glycerol are found to be compatible with basic pigments. In addition, varnishes made from ester copals form hard durable films that show good resistance to water and alkali.<sup>126</sup>

The esterification of copal resins is carried out by the same general methods as those used for colophony but experience is required to avoid difficulty when glycerol is added to the resin.<sup>127</sup> When a mixture of copal and glycerol is heated, it tends to polymerize to an infusible, spongy product. Examples of this phenomenon were observed in the author's laboratory while studying the esterification of Congo copal.<sup>128</sup> For instance Congo resin was run at 327°C. until sufficiently

<sup>122</sup> J. Saphier, *Paint and Varnish Production Mgr.*, 1934, 11 (4), 18; *Chem. Abs.*, 1935, 29, 363.

<sup>123</sup> I. W. Humphrey, U. S. P. 1,877,179, Sept. 13, 1932; *Chem. Abs.*, 1933, 27, 200. R. J. Byrkit, Jr., U. S. P. 1,901,630, Mar. 14, 1933; *Chem. Abs.*, 1933, 27, 3223. I. W. Humphrey, U. S. P. 1,944,241, Jan. 23, 1934; *Chem. Abs.*, 1934, 28, 2020. I. W. Humphrey, U. S. P. 1,961,931, June 5, 1934; *Chem. Abs.*, 1934, 28, 4904. R. J. Byrkit, U. S. P. 1,973,865, Sept. 18, 1934; *Chem. Abs.*, 1934, 28, 7044. All patents to Hercules Powder Co. For hydrogenation of rosin see Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., New York, 1930.

<sup>125</sup> French P. 710,814, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1811. This was also suggested by Humphrey, *loc. cit.* Rosin can be hydrogenated in presence of castor oil to give a non-sticky resin which is usable in soaps. See German P. 451,180, 1922, to Riebeckshe, A. Montanwerke A.-G.; *Brit. Chem. Abs.* B, 1929, 27.

<sup>126</sup> A discussion of varnishes made from copal esters is given in Chapter 39.

<sup>127</sup> For general articles on copal esters see: F. Schlinker, *Synthetic and Applied Finishes*, 1933, 3, 165. Meister, *Farben.-Ztg.*, 1934, 39, 753; *Chem. Abs.*, 1934, 28, 6326. A. Mann, *Farbe u. Lack*, 1934, 146, 158; *Chem. Abs.*, 1934, 28, 3602. E. Stock, *Farben.-Ztg.*, 1934, 39, 141; *Chem. Abs.*, 1934, 28, 3252. T. H. Barry, *Paint Manuf.*, 1932, 2, 215, 254; *Chem. Abs.*, 1932, 26, 6162. H. Brendel, *Farben.-Ztg.*, 1923, 29, 231; *Chem. Abs.*, 1924, 18, 2257. G. Dantlo, *Peintures, pigments, vernis*, 1932, 9, 23; *Brit. Chem. Abs.* B, 1932, 392.

<sup>128</sup> Carleton Ellis and L. Rabinovits, *Ind. Eng. Chem.*, 1916, 8, 406.

soluble in turpentine, and then glycerol added. A vigorous reaction occurred, yielding a spongy product which could not be fused on heating to over 360°C. On cooling, a porous resinous mass was obtained.

In the work of Gardner and Holdt<sup>129</sup> the same tendency to polymerize was encountered and a further study was made of the conditions under which this phenomenon occurs. The effect of metals, which some experimenters had thought to be the cause of polymerization, was eliminated by the use of glass apparatus.

In one of the preliminary experiments Gardner and Holdt heated Congo copal to 315°C and maintained it at that temperature for 30 minutes. During the heating the resin melted completely and appeared to be sufficiently cracked or run. The temperature was dropped to 280°C and 10 per cent of glycerol added. Then the temperature was increased to 290°C to bring about a combination of the resin acids and glycerol. In about 30 minutes the mixture suddenly became thick and gummy, then almost solid, swelling to such an extent as to fill the vessel almost completely. A spongy porous mass was obtained. The resin alone could not be made to polymerize even after prolonged heating in the absence of glycerol, hence the change must be attributed to the presence of the latter.

The polymerization of Manila and Pontianac copals was found to vary in speed but to resemble that of Congo. In each case, indication that gelling was about to take place was a sudden foaming, very similar to, but much more violent than the foaming which sometimes occurs when these resins are being melted.

From further experiments Gardner and Holdt concluded that polymerization would not occur if the resin is completely cracked previous to the addition of glycerol. Congo copal heated for one hour and 30 minutes at 280°C. and then treated with 10 per cent of glycerol did not polymerize. The excess of glycerol used was apparent in the cold solidified resin. Variation in the time of cracking showed that under the laboratory conditions polymerization would not occur if the resin was heated for more than 70 minutes. For a commercial plant, the length of time necessary to crack copal for successful esterification with glycerol must be determined for the individual apparatus at hand. From their work, the experimenters concluded that uncracked copals contain substances that have to be changed or volatilized by heat if polymerization is to be avoided.

Gardner and Holdt followed the progress of esterification by determining the acid number of the melt. Starting with Congo copal that had been cracked 75 minutes and had an acid number of 80 they added 6 per cent glycerol and maintained the mixture at 280°C. The condition of the resin and its acid number at ten-minute intervals is given in Table 38.

TABLE 38.—*Progress of Esterification of Copal.*

Time of Heating with Glycerol	Observations	Acid Value
10 minutes	Much glycerol left uncombined. Product cloudy	42
20 minutes	Some glycerol uncombined. Product somewhat cloudy.	36
30 minutes	Few drops of glycerol on side of flask at end of heating. Product clear.	30
40 minutes	Product clear.	23
50 minutes	Product clear.	19
1 hour	Product clear.	15
2 hours	Product clear but quite dark	5.5

The results show that esterification takes place rapidly at first. The acid value was reduced almost one-half during the first ten minutes of heating. The time

<sup>129</sup> H. A. Gardner and P. C. Holdt, *Circ., Paint Mfrs. Assoc.*, 1922, 151; *Chem. Abs.*, 1922, 16, 3217.



needed for esterification is therefore dependent upon the acid number desired in the product.

Excess glycerol and catalysts also hasten the reaction between copals and glycerol. If excess glycerol is added it must be volatilized after completion of esterification to insure a clear ester. The catalysts suggested were zinc and aluminum.

As a result of their work Gardner and Holdt offered the following procedure for the esterification of Congo copal. Bring the resin quickly to 315-325°C. and hold it there for 75-90 minutes or longer. Lower the temperature to 280°C. and add glycerol in slight excess (6-8 per cent). Raise to 292-295°C. and maintain at that temperature until the desired degree of neutralization has been obtained. After cooling, the ester is either poured into containers and stored or used directly to produce a varnish by heating with oils.

The disadvantages that accompany resins having high acidity have led a number of experimenters to investigate the esterification of copals. A procedure developed by Ellis<sup>130</sup> overcomes the difficulty of polymerization and produces a clear resin. This result was obtained by heating Congo copal for 3.5 hours at 315-325°C. and esterifying at 300°C. with 1/16 of its weight of glycerol in a covered aluminum kettle with a reflux condenser. Using a similar apparatus Ellis and Rabinovitz<sup>131</sup> esterified successfully dammar gum, Congo gum and Pontianac copal. An example from this work is as follows: 92 parts of fused Pontianac copal were heated with 8 parts of glycerol for 5 hours at 260-280°C. The acid number decreased from 74 to 34. A mixture of 100 kilos of cracked Congo copal and 15 kilos of redistilled copal oil were esterified with 5-6 kilos of glycerol by Terrisse.<sup>132</sup> The mass was heated at 280°C. until it was soluble in varnish solvents.

A treatment of copals with phenol and naphthalene before esterification has been suggested by Terrisse.<sup>133</sup> A mixture of copal and phenol or naphthalene is heated in an autoclave at 240-360°C. The phenol or naphthalene is removed finally by distillation and the resulting product is esterified with glycerol. In work by Krumbhaar,<sup>134</sup> on pretreatment of fossil resins, copals were masticated between steam-heated rollers to make them more soluble and fusible. After fusing, the resins are esterified with glycerol.

Brendel<sup>135</sup> proposed to esterify copals in the presence of drying oils. After cracking copals until they were free from foam, glycerol and linseed oil were added and the whole mass was heated to 310°C. Another proposal was the use of higher fatty acids with fossil resins and glycerol. The resin is dissolved in the acid and esterified at 250-280°C. in an inert atmosphere. Oil-soluble products are obtained.<sup>136</sup>

**Esterification of Copals by Other Methods.** Many of the other procedures suggested for esterifying resin have been used also for copals. For instance, the method of heating resins with high-boiling esters has been applied to the preparation of copal esters. This procedure is said to eliminate the thorough running that copals must be given before esterification. The avoidance of long heating at high temperatures produces a better-colored ester.

<sup>130</sup> Carleton Ellis, U. S. P. 1,242,161, Oct. 9, 1917, to Ellis-Foster Co. and Indestructible Paint Co., Ltd.

<sup>131</sup> Carleton Ellis and I. Rabinovitz, *Ind. Eng. Chem.*, 1916, 8, 406.

<sup>132</sup> H. Terrisse, *Chem. Umschau*, 26, 194; *Chem. Abs.*, 1920, 14, 2720. See also H. Terrisse, U. S. P. 1,236,996, Aug. 14, 1917; *Chem. Abs.*, 1917, 11, 2967.

<sup>133</sup> H. Terrisse, British P. 23,055, 1914, to Indestructible Paint Co., Ltd.; *J. S. C. I.*, 1916, 35, 57. For work on "solubilizing" of resins see H. Terrisse, British P. 14,544, 1903; *J. S. C. I.*, 1904, 23, 552. U. S. P. 882,842, Apr. 7, 1908, to Fabr. de vernis et prod. chim.; *Chem. Abs.*, 1908, 2, 2457.

<sup>134</sup> W. Krumbhaar, *Official Digest, Federation Paint, Varnish Production Clubs*, 1934, 134, 43. *Chem. Abs.*, 1934, 28, 2550.

<sup>135</sup> H. Brendel, *Farben.-Ztg.*, 1923, 29, 231; *Chem. Abs.*, 1927, 21, 182.

<sup>136</sup> German P. 575,199, 1933, to Firma Louis Blumer; *Chem. Abs.*, 1933, 27, 3629.

Esters that boil above 200°C. and whose resulting acids are volatile at that temperature are desirable. Following this principle, Hesse<sup>137</sup> employed alkyl or aryl esters of phthalic acid. Equal parts of copal and diethyl phthalate were mixed and the lower-boiling products removed by distillation. Other esters possessing the desired characteristics have been proposed. For instance, benzyl acetate or dibutyl phthalate is heated with copal at 300°C. for 4 hours. The acetic or phthalic acid is driven off as it is formed. The copal benzyl ester, melting at 43-52°C., has an acid number of 20.6 and a saponification number of 105. Products of alleged therapeutic value are prepared by heating compounds of the general formula,  $R_1CONR_2R_3$ , with copal. For example, acetamide and Congo copal react at 300°C. to give copalamide.<sup>138</sup> By the same general methods, Fonrobert and Lemmer<sup>139</sup> made Congo copal benzyl ester, Congo copal glycerol ester, Kauri copal benzyl ester and Manila copal butyl ester. The preparation of Congo glycerol ester is given as follows: 250 g. of Congo copal are heated with 147 g. of stearic triglyceride for 4 hours at 300°C. The copal is melted without vigorous frothing and at 275°C. a calm-boiling melt is formed. At the end of the esterification the stearic acid formed by the reactions is removed by heating at 260°C. under a vacuum of 10 mm. The residue consisted of 233 g. of Congo copal glycerol ester having an acid number of 1.5.

Copal may be treated with a number of other substances to give resins with special properties. Schaal<sup>140</sup> proposed that phenol, cresol, resorcinol, or naphthol be esterified with copal by heating at 180-210°C. The resulting resins were said to be usable in quick-drying varnishes. Scheiber<sup>141</sup> dissolved Manila copal in caustic alkali and mixed this with an alkaline solution of a polyhydroxy-carboxylic aliphatic acid (trihydroxystearic acid, dihydroxypalmitic acid). The resin is precipitated by adding hydrochloric acid. After filtering, the product is heated to 150°C. Since the resin is soluble in alcohol it has been suggested as a shellac substitute. It is rendered insoluble and infusible by heat. A rubber-like mass that is soluble in rubber solvents was obtained by Zobel<sup>142</sup> from creosote oil and copal. A mixture of hard-wood creosote oil and copal was heated and the resulting solution poured into petroleum naphtha.

**Esterification of Mixtures of Copal and Rosin.** Esterification of a mixture of copal and rosin overcomes the difficulties encountered with pure copal and at the same time a resin superior to ester gum is produced. The necessity of running copal completely creates problems that can be avoided if there is some rosin present. Also, the cracking is decisively aided and esterification of copal appears to be facilitated by the presence of rosin. The percentage of rosin present is generally greater than that of copal in order to keep the fusion point low. The addition of a hard fossil resin to rosin makes the final varnish films harder and more durable.

Mixed esters of copal and colophony were prepared by Schaal.<sup>143</sup> He proposed using glycerol, fruit sugar, phenol, cane sugar and mannitol with a mixture of

<sup>137</sup> A. Hesse, U. S. P. 1,003,741, Sept. 19, 1911; *J.S.C.I.*, 1911, 30, 1223. German P. 227,667, 1909; *J.S.C.I.*, 1910, 29, 1398.

<sup>138</sup> German P. 555,812, 1929, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1932, 26, 5964. British P. 353,616, 1930; *Brit. Chem. Abs. B*, 1931, 1019. German P. 578,827, 1933; *Chem. Abs.*, 1934, 28, 918.

<sup>139</sup> E. Fonrobert and F. Lemmer, U. S. P. 1,952,367, Mar. 27, 1934, to Resinous Products & Chemical Co.; *Chem. Abs.*, 1934, 28, 3606.

<sup>140</sup> E. Schaal, British P. 12,807, 1894; *J.S.C.I.*, 1896, 5, 523. German P. 75,119, 1890; *Chem. Zentr.*, 1894, 2, 884. German P. 75,126, 1891; *Chem. Zentr.*, 1894, 2, 884.

<sup>141</sup> J. Scheiber, U. S. P. 1,938,468, Dec. 5, 1933, to W. Dux; *Chem. Abs.*, 1934, 28, 1207. U. S. P. 1,903,506, Apr. 11, 1933; *Chem. Abs.*, 1933, 27, 3350. British P. 350,764, 1929; *Chem. Abs.*, 1932, 26, 3124. German P. 551,099, 1929; *Chem. Abs.*, 1932, 26, 4487.

<sup>142</sup> F. C. Zobel, U. S. P. 1,786,281, Dec. 23, 1930; *Brit. Chem. Abs. B*, 1931, 771.

<sup>143</sup> E. Schaal, U. S. P. 501,446, July 11, 1893. See also E. Schaal, German P. 75,119 and 75,126, 1891; *Chem. Zentr.*, 1894, 2, 884.

copal and rosin. An example given by him is as follows: Fifty pounds of Manila copal are melted and an equal amount of rosin added. The temperature is raised to 180-210°C. and 6 pounds each of fruit sugar and glycerol are gradually added. The mixture is stirred constantly. The temperature is slowly increased to 280°C. and a vacuum of 100 mm. is maintained to remove aqueous vapors.

The esterification of mixtures of Congo copal and rosin was studied by Murray.<sup>144</sup> He found that 10 per cent of copal improved the hardness and toughness of the resulting ester without greatly increasing the difficulty of esterification. The process calls for heating a mixture of Congo and rosin in a covered kettle at 316-321°C. After the copal has dissolved completely in the rosin, the batch is cooled to 288°C. and 12 parts of glycerol are added. The reaction with glycerol is permitted to proceed until the desired acidity is reached. With the proportions 2 or 3 parts of copal to 1 part of rosin, the Congo resin tended to polymerize. The experimenter had less polymerization difficulty with an aluminum kettle than with one of copper.

Gammay added a powdered fossil resin to fused colophony and heated until a homogeneous solution resulted and then esterified the mixture with polyhydric alcohols.<sup>145</sup> Ellis and Weber<sup>146</sup> used a mixture of 4-5 parts of Congo with 1-2 parts of rosin. The mixture is heated until fusion occurs, glycerol added and esterification carried out at 270-290°C. The presence of calcium resinate aids the reaction.

Hocker<sup>147</sup> proposed that baking-varnishes be prepared from combinations of copals, rosin oil, gelatinizable vegetable oil, rosin and glycerol. The procedure for one method is given as follows: Two parts of rosin oil are heated with 1 part of Congo copal at 300°C. until the resin is completely fused. One gallon of glycerol for each 14 pounds of copal is added and the temperature maintained at 300°C. for one hour. The resin may be fused alone, with rosin or with tung oil before incorporation with glycerol and rosin oil. Also, the rosin oil may be incorporated with the drying oil and then heated with the esterified copal.<sup>148</sup>

#### APPARATUS EMPLOYED IN ESTERIFICATIONS

In the early attempts to prepare ester gum open vessels were used but the water formed during the esterification process vaporizes quickly and carries away much of the unreacted glycerol. This results in esters with high acid numbers. However, the water must be allowed to escape. The best procedure is to use a closed kettle with an air condenser of such length that it condenses the glycerol while permitting the steam to escape. By this method a large excess of glycerol is not needed (2 per cent excess is the general practice).

The esterification is carried out in both copper and aluminum equipment but aluminum is generally preferred. At 250°C. the esterification of rosin takes 3-5 hours. On cooling, boric acid is often added to inhibit the hydrolysis of the ester.<sup>149</sup>

The type of plant suggested by Schaal is shown in Figure 121. The kettle is equipped with a charging funnel and stirring device. A gooseneck connects the kettle to a receiver. The outlet pipe in the top of the receiver is connected with a pump so that a partial vacuum can be maintained.

<sup>144</sup> A. Murray, *Chem. Met. Eng.*, 1921, 25, 474.

<sup>145</sup> H. Gammay, British P. 386,179, 1933, to Chemicon A.-G.; *Chem. Abs.*, 1933, 27, 4490 French P. 734,893, 1932; *Chem. Abs.*, 1933, 27, 1219.

<sup>146</sup> Carleton Ellis and H. M. Weber, U. S. P. 1,381,863, June 14, 1921, to Ellis-Foster Co.; *Chem. Abs.*, 1921, 25, 3560.

<sup>147</sup> C. D. Hocker, U. S. P. 1,634,359, July 5, 1927, to Western Electric Co.; *Chem. Abs.*, 1927, 21, 2993.

<sup>148</sup> C. D. Hocker, U. S. P. 1,638,579, Aug. 9, 1927, to Western Electric Co.; *Chem. Abs.*, 1927, 21, 3276.

<sup>149</sup> For a description of manufacturing methods employed outside of the United States see H. Hadert, *Farben.-Chem.*, 1934, 5, 409; *Brit. Chem. Abs. B*, 1935, 33.

The apparatus used by the author for experimental work is shown in Figure 122. It consists of an aluminum kettle fitted with a tight cover and stirrer. The

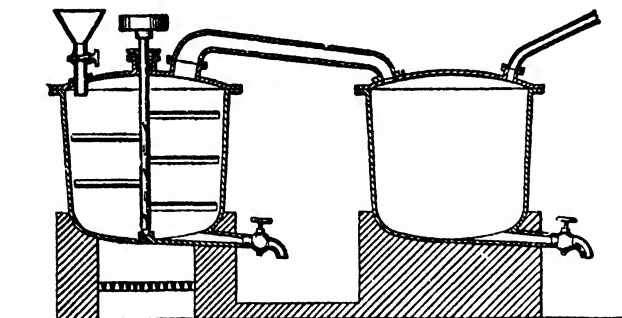


FIG 121.

Schaal's Apparatus.

apparatus was mounted on a truck so that it could be moved on or off the fire without interrupting the stirring, hence being very convenient to handle.

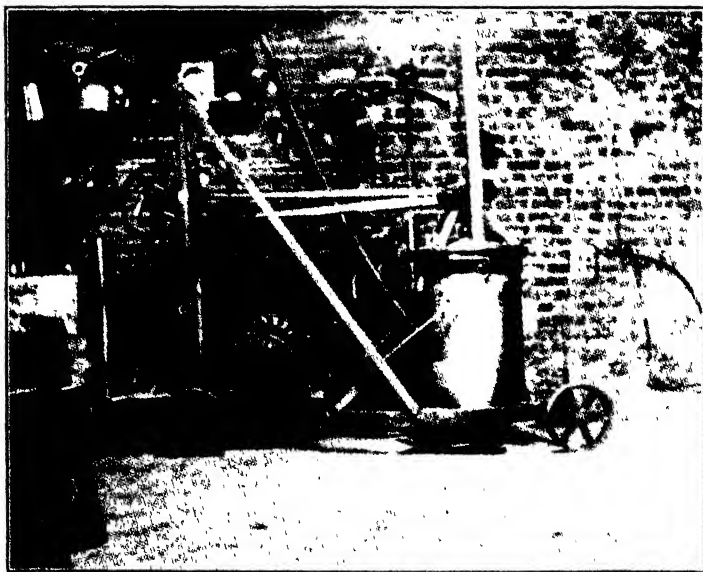


FIG. 122.—Apparatus Employed by the Author for Esterification of Natural Resins.

Sommer<sup>120</sup> proposed an apparatus with a cover, tubular reflux condenser, foam distributor, stirrer, and inlets for glycerol, inert gas, and air. The design allows for removal of dirt from the bottom. The ester is discharged by pressure.

Bergmann<sup>121</sup> has described a German plant for esterifying copal resins in which 400-4000 kilos of copal are treated in one operation to produce 1200 to 12,000

<sup>120</sup> J. Sommer, British P. 319,651, 1929; *Brit. Chem. Abs.* B, 1930, 677. German Design P. 1,049,805, 1926.

<sup>121</sup> A. Bergmann, *Peintures, pigments, vernis*, 1931, 8, 1472; *Chem. Abs.*, 1931, 25, 3854.

kilos of varnish. The whole process is conducted in an atmosphere of carbon dioxide.<sup>102</sup>

In order to minimize fume loss in the running and esterification of natural resins, Frenkel<sup>103</sup> suggested the use of an apparatus heated indirectly with a high-boiling liquid medium (e.g., a mixture of phenyl ether and biphenyl) circulated through jacketed kettles. To obtain a good-quality ester an aluminum vessel is employed and an inert atmosphere is maintained.

#### ESTERIFICATION OF OTHER RESINS

The esterification of other resins has been undertaken with an idea of improving them for their present uses or of modifying them so that their field of application is widened. Although experimental details for the esterification of each resin will probably have to be determined individually, the methods discussed under rosin are generally applicable to other resins.

A number of these methods have been used to esterify shellac. Harries and Nagel<sup>104</sup> heated shellac with methyl alcohol in the presence of hydrochloric acid to obtain a methyl ester of shellac in the form of a yellow syrup. This syrup was purified by treatment with ether and crystallized from ethyl acetate. The final product melted at 149°C. and was soluble in alcohol, chloroform and benzene; slightly soluble in ether; and insoluble in petroleum ether. The same workers prepared a diacetyl ester by heating shellac with acetic anhydride.

Ethylene oxide, propylene oxide or corresponding halogen hydrins have also been proposed as esterifying agents for shellac. In these reactions the temperature is held at 60-100°C. and an increase in pressure is desirable. Boric acid and zinc chloride are catalysts for the esterification.<sup>105</sup>

The esterification of shellac with glycerol and the incorporation of the resulting resin in drying oil to make a baking enamel was suggested by Hocker.<sup>106</sup> Litharge and rosin added to glycerol and shellac aid in the production of a substance that can be used with oils.<sup>107</sup> Fusion with glycerol has been employed as a means for reconditioning shellac that has lost its fusibility through contact with bleaching powder. To accomplish this end, shellac is heated with glycerol at 160-220°C.<sup>108</sup>

The incorporation of shellac with glycerol, rosin and drying oils has been studied by Aldis.<sup>109</sup> The mixture is heated at 230-280°C. and then diluted with hot oil to give a long oil varnish. In another procedure glycerol and drying oil were replaced with ethylene glycol and castor oil to make a substance to be employed as a plasticizer in lacquers.<sup>100</sup>

Dammar is another resin which has been esterified with glycerol. In an experiment performed in the author's laboratory 50 parts of dammar and 5 parts of glycerol were heated with stirring at 250°C. for 30 minutes, yielding a dark-colored resin. The acid number fell from 39 to 12.5. Brendel<sup>101</sup> obtained best results with 2 per cent glycerol. The dammar and glycerol mix was heated at 180-270°C.

<sup>102</sup> H. Rahder, (*Farben.-Ztg.*, 1926, 31, 1742; *Brit. Chem. Abs.*, B, 1926, 554) has noted the need of an inert atmosphere in running and esterifying copals. See also Meister, *Farben.-Ztg.*, 1932, 37, 1604; *Chem. Abs.*, 1932, 26, 5776 and M. Bottler, *Kunststoffe*, 1913, 3, 85.

<sup>103</sup> H. L. Frenkel, *British P.* 419,952, 1933; *Brit. Chem. Abs.* B, 1935, 111.

<sup>104</sup> C. Harries and W. Nagel, *Ber.*, 1922, 55, 3833; *Chem. Abs.*, 1923, 17, 1007 *Kolloid-Z.*, 1923, 33, 247; *Chem. Abs.*, 1924, 18, 1057.

<sup>105</sup> *British P.* 328,190, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 677.

<sup>106</sup> C. D. Hocker, *U. S. P.* 1,638,579, Aug. 9, 1927, to Western Electric Co.; *Chem. Abs.*, 1927, 21, 3276.

<sup>107</sup> H. Hadert, *Farben.-Chem.*, 1934, 5, 328; *Brit. Chem. Abs.* B, 1934, 931.

<sup>108</sup> V. M. Ivanof, *Russian P.* 3,853, 1927; *Chem. Abs.*, 1928, 22, 4644.

<sup>109</sup> R. W. Aldis, *Bull. Indian Lac. Research Inst.*, 1933, 12; *Chem. Abs.*, 1933, 27, 2828.

<sup>100</sup> R. W. Aldis, *Research Note, Indian Lac. Inst.*, 1933, 5; *Chem. Abs.*, 1933, 27, 2829.

<sup>101</sup> H. Brendel, *Farben.-Ztg.*, 1924, 29, 1693; *Chem. Abs.*, 1925, 19, 408. *Farbe u. Lacke*, 1926, 31, 297, 310; *Chem. Abs.*, 1927, 21, 182.

With this proportion of glycerol the final resin was free from the tackiness and brittleness of dammar and could be used for outdoor work. When the proportion of glycerol was increased to 8 per cent poor results were obtained.

Humphrey<sup>155</sup> esterified sandarac and pontianac gums with aliphatic chloroethers in presence of alkalis and monohydric alcohols. Esters of pimic acid may be prepared by heating under pressure with methyl alcohol, glycerol, or glycol in the presence of 3 per cent p-toluenesulphonic acid.<sup>156</sup> Pinene, turpentine and camphene can be converted into esters by using polycarboxylic anhydrides and aluminum chloride. A mixture of these substances is heated with a dehydrating catalyst (e.g., zinc chloride, boron trioxide) to give the ester.<sup>154</sup>

The conversion of cherry gum into a balsam-like material for varnishes was suggested by Voss.<sup>155</sup> The change is brought about by treating the gum with pyridine and amyl alcohol.

#### MISCELLANEOUS ESTERIFICATIONS

Natural substances of the type of montan wax have been esterified for the purpose of improving their properties so that they can compete with more expensive products used in polishes and in plastic compositions.

Montan wax may be esterified directly with glycerol. For example: 100 kg. of montan wax and 25 kg. of glycerol were heated until the wax had a low acid number. The time of reaction is shortened by using an autoclave, and sulphuric or hydrochloric acid as catalysts. The product had a melting point of 80-81°C. and had the property of raising the melting points of fats and waxes of lower melting points.<sup>156</sup> The wax may be bleached before esterification.<sup>157</sup> A wax, to be used in polishes, is prepared by partial esterification with glycerol and conversion of the remaining wax acids into metal salts by the addition of inorganic oxides.<sup>158</sup>

Glycerol may be replaced by monohydric alcohols to give waxes that can be employed as a basis for polishes. Excess alcohol is added and the unreacted portion removed by distilling.<sup>159</sup> Esterification products of ethylene glycol with such waxes have been used with fillers to make molded articles.<sup>170</sup> The esterification of bleached montan wax with glycerol in presence of a siccative, sulphur or sulphur compounds yields plastic compositions.<sup>171</sup>

Modification of the properties of montan wax may follow a different path. For example, the acids of the bleached wax may be reduced to alcohols and then esterified with organic acids. Non-aromatic monocarboxylic acids containing up to 25

<sup>155</sup> I. W. Humphrey, U. S. P. 1,843,284, Feb. 2, 1932, to Hercules Powder Co.; *Brit. Chem. Abs.* B, 1932, 1042.

<sup>156</sup> A. C. Johnston, U. S. P. 1,840,395, Jan. 1, 1932, to Hercules Powder Co.; *Brit. Chem. Abs.* B, 1932, 1042.

<sup>154</sup> H. A. Bruson, U. S. P. 1,896,007, Feb. 7, 1933, to Resinous Products and Chemical Co.; *Brit. Chem. Abs.* B, 1933, 905.

<sup>155</sup> A. Voss, German P. 414,258, 1922, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1926, 44, 816B.

<sup>156</sup> German P. 244,786, 1912, to E. Schliemanns Export-Ceresin-Fabrik G.m.b.H.; *Chem. Abs.*, 1912, 6, 2313.

<sup>157</sup> W. Pungs and M. Jahrstorfer, U. S. P. 1,737,395, Dec. 3, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 948. The wax bleached by oxygen or by chromic acid generally contains a good proportion of fatty acids.

<sup>158</sup> F. W. Guthke and W. Pungs, U. S. P. 1,884,056, Dec. 1, 1932; *Chem. Abs.*, 1932, 26, 1099. German P. 558,437, 1927; *Chem. Abs.*, 1933, 27, 386. W. Pungs and M. Jahrstorfer, German P. 563,394, 1927; *Chem. Abs.*, 1933, 27, 1117. All patents to I. G. Farbenind. A.-G. For further work on the addition of inorganic substances see German P. 564,488, 1928, to Deutsche Hydrierwerke A.-G.; *Chem. Abs.*, 1933, 27, 1117.

<sup>159</sup> W. Pungs and H. Freytag, U. S. P. 1,972,459, Sept. 4, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6584. German P. 570,837, 1933; *Chem. Abs.*, 1933, 27, 4434.

<sup>170</sup> British P. 376,276, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 949. Esters may be used as esterifying agents. See British P. 356,731, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4243.

<sup>171</sup> M. Luther and R. Held, German P. 575,954, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4890. French P. 676,091, 1929; *Chem. Abs.*, 1930, 24, 2846.

carbon atoms (e.g., formic, acetic, stearic, palmitic, linoleic, abietic) have been recommended. By the proper selection of acid, waxes of desired melting point can be prepared, some of which exhibit physical properties similar to carnauba or beeswax.<sup>173</sup> Wax alcohols are proposed as esterifying agents for the distillation residues of fatty oils or acids. The residues are esterified with these alcohols and then neutralized with litharge. The product is diluted with turpentine or benzine to give a quick-drying varnish.<sup>173</sup> Esterified wax may be treated with a nitrogenous base (e.g., ethanolamine, piperidine, aryl- or alkyl amines) at 200°C. to convert part of the esters into amides. The products have been suggested for polishes and textile finishes.<sup>173a</sup>

Luther and Beller<sup>174</sup> have reported the formation of rubber-like masses from the heating of sulphur monochloride with a mixture of esters of polyhydric alcohols and unsaturated fatty acids, which were obtained from bleached waxes. A similar mixture may be treated with oxygen at 100°C. in the presence of litharge to give a product resembling linnoxyn.<sup>175</sup> Acids from montan wax, soya bean oil, linseed oil or tung oil were esterified with sorbitol to give a viscous drying oil.<sup>176</sup>

<sup>172</sup> W. Pungs and M. Jährstorfer, U. S. P. 1,942,833, 1934, *Chem. Abs.*, 1934, 28, 1824. German P. 559,631, 1930, *Chem. Abs.*, 1933, 27, 860. British P. 362,632, 1930, *Brit. Chem. Abs.* B, 1932, 270. All patents to I. G. Farbenind. A.-G.

<sup>173</sup> F. Brosel, German P. 579,467, 1933, to Vereinigte Farben und Lackfabriken; *Chem. Abs.*, 1933, 27, 4699.

<sup>173a</sup> British P. 415,769, 1933, to I. G. Farbenind. A.-G., *Brit. Chem. Abs.* B, 1934, 971.

<sup>174</sup> M. Luther and H. Beller, U. S. P. 1,897,133, Feb. 14, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2845.

<sup>175</sup> M. Luther and H. Beller, U. S. P. 1,901,374, Mar. 14, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3094.

<sup>176</sup> British P. 350,992, 1929, to I. G. Farbenind. A.-G., *Brit. Chem. Abs.* B, 1931, 819.

# Chapter 39

## Uses of Natural Resin Esters

### ESTER GUM VARNISHES

As was pointed out in Chapter 37 the use of rosin in oil varnishes is objectionable because of its acid nature, its softness, its lack of durability and its poor resistance to water. Ester gum represents a decided improvement over both raw and limed rosin with respect to water-resistance, durability and freedom from livering. The discovery that a good waterproof varnish can be made from a mixture of tung oil and ester gum has created a noteworthy change in varnish making. The result has been the substitution of ester gum for copals in the manufacture of spar varnishes. In fact, in numerous instances specifications for such varnishes have been modified so that ester gum is preferred to a hard fossil resin.

In addition to the wide use of ester gum in oil varnishes, this ester is employed to some extent in nitrocellulose lacquers. This is possible because ester gum is freely compatible not only with nitrocellulose but also with the majority of lacquer solvents and plasticizers. Coatings containing ester gum can be classified roughly into three groups, the first being the most important: 1. Oil varnishes, 2. Cellulose lacquers, 3. Spirit varnishes.

Other resin esters, particularly copal esters, are employed to some extent in oil varnishes, but ester gum is the most widely used resin ester.<sup>1</sup>

Ester gum in tung oil gives a much better varnish than the same resin in linseed oil. Tung oil appears to be more or less specific with the rosin ester, the oil imparting the required water-resistance to the coating. Hence, extensive use has been made of these two ingredients to manufacture a relatively cheap and yet entirely satisfactory varnish. In general an ester gum for oil varnishes should be pale in color and should have an acid number of about 6-10. According to Sanderson<sup>2</sup> there is some demand for ester gum with an acid number of 15, the slight acidity being necessary to assist the solvent action for polymerized tung oil and to increase the capacity for wetting pigments.

Some typical formulas for the preparation of oil varnishes in which ester gum is used have already been given in Chapter 38 in order to illustrate the esterification of rosin in the presence of drying oils.<sup>3</sup> There are of course many other varnishes in which ester gum is employed and a few are cited below.

A formula for the preparation of ester gum spar varnish containing free rosin, as employed in one varnish plant, is the following:

Tung oil	45 gal.
Linseed oil	5 gal.
Ester gum	100 lbs.
Rosin	50 lbs.
Litharge	1 lb.
Cobalt acetate	¼ lb.

<sup>1</sup> Advantages of copal esters over raw copals as pointed out by Meister (*Farben-Ztg.*, 1934, 39, 753; *Brit. Chem. Abs. B*, 1934, 803) include increased solubility in oils and thinners, improved weather-resistance of films, retardation of blooming and reduced livering with basic pigments. Copal-ester films bleach on exposure and do not display after-yellowing.

<sup>2</sup> J. McE. Sanderson, *Ind. Eng. Chem.*, 1934, 26, 711.

<sup>3</sup> See the section entitled "Esterification in Presence of Drying Oils" in Chapter 38.



To this mixture is added 50 per cent by volume of thinner composed of three parts of turpentine and one part of heavy benzine or mineral spirits.

The tung oil may be either raw or "prepared." The prepared oil is made by heating tung oil to 200°C. for 15 hours and then allowing it to settle to remove albuminous matter. The use of the small proportion of linseed oil is considered desirable because the varnish is said to be rendered more elastic thereby. The rosin is added to assist in blending the various ingredients. It is stated that the above proportion of rosin does not detract materially from the waterproof qualities of the varnish.

In preparing the varnish the linseed oil and tung oil are mixed and heated to 150°C. Litharge is then added and the temperature is raised and maintained at 230°C. to body the oil. When the oil begins to thicken, the rosin and ester gum are added and the temperature is raised to 300-315°C. The kettle is now pulled from the fire and allowed to cool. When the temperature has fallen to about 230°C. the cobalt acetate is added. The thinner is incorporated with the varnish at a temperature of 215°C.

This is of course by no means the only procedure for incorporating tung oil in varnishes. For instance in a method described by Riemann<sup>4</sup> the resin is not cooked with the oil from the beginning of the varnish-making operation. Instead, the oil is heated to 220-250°C. and then added to the resin which has been previously heated to 320-340°C. Driers and thinners are incorporated during the cooling operation.

A varnish, stated to be quick-drying, was prepared by Kessler<sup>5</sup> from the following ingredients:

Ester gum	7.5 per cent
Fused kauri gum	7.5
Tung oil	3.0
Boiled linseed oil	2.0
Benzene.	20.0
Toluene.	25.0
Xylene.	25.0
Butyl alcohol	10.0

This varnish is intended for use on metal work and is applied either by brushing or dipping.

The employment of copal esters in varnishes is exemplified by a coating preparation used by Terrisse.<sup>6</sup> Glycerol-esterified Manila copal is heated to 300°C. and then mixed with half its weight of linseed oil. When all the oil has been incorporated the temperature is raised to 310°C. and maintained at that point until the mixture has the desired consistency. Driers and thinners are added when the mix is being cooled. A paint said to have good covering power is obtained by grinding equal parts of the varnish and zinc oxide in a ball mill.

In addition to linseed oil and tung oil some of the lesser-known oils have been used favorably in ester-gum varnishes. For instance a varnish is prepared by heating a mixture of ester gum and paulownia oil to a high temperature and adding naphthols or naphthylamines and resinate driers.<sup>7</sup> Matumoto<sup>8</sup> obtained a paint by heating paulownia oil with fatty acids of the oil and with ester gum and then adding litharge and pigments. Experiments performed by Sward<sup>9</sup> indicated that an ester-gum varnish prepared with oiticica oil compares quite favorably with a similar varnish using tung oil.<sup>10</sup>

<sup>4</sup> F. Riemann, *Farbe u. Lack*, 1929, 6; *Chem. Abs.*, 1929, 23, 1761.

<sup>5</sup> J. M. Kessler, U. S. P. 1,642,155, Sept. 13, 1927, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1927, 21, 3756.

<sup>6</sup> H. Terrisse, U. S. P. 1,214,611, Feb. 6, 1917, to the Indestructible Paint Co., Ltd.; *Chem. Abs.*, 1917, 13, 1047.

<sup>7</sup> T. Hagiya, Japanese P. 93,602, 1931, to Teikoku Toryo K. K.; *Chem. Abs.*, 1933, 27, 1529.

<sup>8</sup> G. Matumoto, Japanese P. 93,213, 1931, to Ititaro Syozai; *Chem. Abs.*, 1933, 27, 1528.

<sup>9</sup> G. G. Sward, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1931, 377, 120; *Chem. Abs.*, 1931, 25, 1689.

<sup>10</sup> Oiticica oil is extracted from the oval-shaped nuts of *Conepia grandifolia* (occurring in Brazil). It

The results of several investigations on the phenomena associated with varnish-cooking tend to show that ester gum retards the rate of polymerization of both linseed oil and tung oil.<sup>11</sup> The effect is only half as great with ester gum as with raw rosin, however.

**Properties of Ester Gum Films.** That the films formed by ester gums are satisfactory is well authenticated by their long-continued use. Many of the standard varnishes giving satisfactory service contain ester gum as the principal resin and some of these approximate the varnishes prepared from more costly fossil resins. The ester gum films are durable, show good resistance to abrasion and withstand outdoor exposure. When ester gum is mixed with basic pigments to make enamels the product does not liver or thicken.

An idea of the durability of ester gum varnishes may be obtained from the experimental results of Pearce<sup>12</sup> on outdoor exposure tests of various coatings. Some of these results are given in Table 39.

TABLE 39—*Exposure Tests of Varnishes.*

Composition	Gallons of Oil to 100 Pounds of Resin	First Appearance of Cracks in Days		Complete Failure in Days	
		Spring	Fall	Spring	Fall
Rosin-tung linseed . . .	20	29	28	106	100
Ester-tung linseed . . .	20	28	36	134	92
Kauri . . . . .	30	42	64	206	202
Manila-linseed . . . . .	30	36	22	120	203
Ester-tung . . . . .	30	58	100	183	208
Congo-tung linseed . . .	30	43	21	203	141
Rosin-tung perilla . . . .	30	43	36	100	71
Ester-tung . . . . .	40	71	64	134	203
Kauri-linseed . . . . .	40	42	78	141	252

The results indicate that the tung oil-ester gum varnish films do not crack as early as others and that a linseed oil-Kauri coating is the only one showing better results with respect to complete failure. The behavior of ester gum in rust-inhibitive primers was observed by exposure tests of one-year duration. With the pigments that were tried, ester gum proved to be a satisfactory resin.<sup>13</sup>

Experience has shown that films formed from ester gum compositions withstand well the action of water. All of the tung oil-ester gum varnishes obtained by Beegle<sup>14</sup> exhibited good waterproof qualities. However, those made from resins possessing acid numbers below 20 gave the best results when applied to glass and immersed in water 4 days. That the addition of ester gum improves the resistance of an oil film to water was deduced from the experimental work of Serb-Serbin.<sup>15</sup> In a study of permeability of coatings to moisture, Gettens<sup>16</sup> found that those produced from ester gum were among the best. Enamels containing ester gum are likely to chalk, blister and remain sticky for a long time under tropical conditions, probably because of the high humidity and temperature.<sup>17</sup> The difficulties were reduced by using an Albertol primer.

is said to resemble tung oil in many respects. See E. R. Bolton and C. Revis, *Analyst*, 1918, 43, 251; *Chem. Abs.*, 1918, 12, 2056. H. A. Gardner, *Circ., Am. Paint Mfrs. Assoc.*, 1923, 177, 220; *Chem. Abs.*, 1923, 17, 2512. Paulownia oil is a Japanese oil that occurs in the seeds of *Paulownia imperialis*. For the properties of this oil see J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan & Co., London, 5th Ed., 1914, II, 83.

<sup>11</sup> H. E. Hofmann, *Ind. Eng. Chem.*, 1925, 17, 175. V. H. Turkington, R. C. Shuey and W. H. Butler, *ibid.*, 1931, 23, 791. R. L. Houck, *Paint, Oil, Chem. Rev.*, 1928, 86 (21), 10; *Chem. Abs.*, 1929, 23, 5336. See also F. H. Rhodes and T. J. Potts, *Chem. Met. Eng.*, 1923, 29, 533. J. Scheiber and O. Nouvel, *Z. angew. Chem.*, 1923, 36, 353; *Chem. Abs.*, 1923, 17, 3104.

<sup>12</sup> W. T. Pearce, *Ind. Eng. Chem.*, 1924, 16, 632.

<sup>13</sup> *Circ., Nat., Paint, Varnish and Lacquer Assoc.*, 1934, 471, 343; *Brit. Chem. Abs. B*, 1935, 31.

<sup>14</sup> F. M. Beegle, *Ind. Eng. Chem.*, 1924, 16, 953. For the preparation of these varnishes see Chapter 38.

<sup>15</sup> P. W. Serb-Serbin, *Malyar. Delo*, 1931 (5, 6), 62-75; *Brit. Chem. Abs. B*, 1934, 333.

<sup>16</sup> R. J. Gettens, *Tech. Studies Field Fine Arts*, 1932, 1, 63; *Chem. Abs.*, 1933, 27, 433.

<sup>17</sup> Arnold, *Chem.-Ztg.*, 1932, 56, 55; *Chem. Abs.*, 1932, 26, 2606.

The yellowing of white enamels was studied by Munzert.<sup>18</sup> Starting with 4 pigments and 4 vehicles, coatings were made and applied to tin-plate panels. After exposure to diffused daylight for 4 days, one-half of the surface was covered with black paper and the panel exposed to sunlight for 14 days. Yellowing occurred in the half that was covered. With the ester gum enamels the yellowing was only slight.

**Properties of Copal Esters.** The properties of copal esters and the films formed from them are, as a whole, excellent. The copal esters are oil-soluble resins that give hard durable films. The coatings show good resistance to water and alkali. If the acid number of the ester is below 20 the esters are reasonably compatible with basic pigments.

In an experiment on resistance to alkalis, Gardner and Holdt<sup>19</sup> coated panels with varnishes containing copals and copal esters. These panels were immersed in 4 and 20 per cent caustic soda solution for 1 week. The copal varnishes were badly affected, being covered with a white scum. The coatings made with copal esters were not attacked by either solution. From a study of synthetic finishes, Staudermann<sup>20</sup> concluded that oil varnishes produced from copal esters are more durable than those obtained from ester gum but that the copals require a longer time to dry.

As has been stated previously, resins of high acid numbers liver or thicken when incorporated with basic pigments. Copal esters with low acid number would be expected to make enamels with pigments such as zinc oxide without this difficulty. Working on this problem, Gardner and Holdt<sup>21</sup> employed a copal ester to prepare varnishes having acid numbers of 4 and 25. Zinc oxide was ground with both varnishes. After standing a few hours the varnish possessing the higher acid number had thickened, but the other one was still of proper consistency after 8 months.

**Insulating Varnishes.** The utilization of ester gum for the manufacture of insulating varnish for coating electrical conductors has been proposed by many workers. Hocker<sup>22</sup> produced such coatings from rosin oil, glycerol, tung oil and ester gum. The product is thinned with benzene to give a quick-baking composition. The incorporation of a sulphide or selenide during the process of esterification is considered advantageous by Ohta.<sup>23</sup> An insulating varnish was prepared as follows: 1000 parts of rosin, 50-150 parts of glycerol, 5-30 parts of sodium sulphide or selenide and 1500 parts of tung oil containing an aluminum catalyst were heated to 240-300°C. After cooling, pigments and thinners were added.

An insulating varnish of different composition was made by Wright,<sup>24</sup> who used the reaction product of gum accroides, rosin and glycerol. Ester gum-tung oil varnishes were found to possess no advantage over rosin-tung oil ones for baked insulators, according to Mizushima.<sup>25</sup>

An electrical-insulating material has been made by cementing mica foil to paper. The glue suggested was produced by heating tung oil, Manjak asphalt, glycerol and

<sup>18</sup> H. Munzert, *Farben.-Ztg.*, 1928, 33, 2849; *Brit. Chem. Abs.* B, 1928, 719

<sup>19</sup> H. A. Gardner and P. C. Holdt, *Circ., U. S. Paint Mfrs. Assoc.*, 1922, 151; *Chem. Abs.*, 1922, 16, 3217.

<sup>20</sup> A. E. Staudermann, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1929, 356, 815; *Brit. Chem. Abs.* B, 1930, 68.

<sup>21</sup> H. A. Gardner and P. C. Holdt, *Circ., U. S. Paint Mfrs. Assoc.*, 1922, 151; *Chem. Abs.*, 1922, 16, 3217.

<sup>22</sup> C. O. Hocker, U. S. P. 1,634,339, July 5, 1927, to Western Elec. Co.; *Chem. Abs.*, 1927, 21, 2893. U. S. P. 1,638,579, Aug. 9, 1927; *Chem. Abs.*, 1927, 21, 3276. British P. 238,696, 1924, to Western Elec. Co., Ltd.; *Chem. Abs.*, 1927, 21, 3276. For the preparation of these compositions see Chapter 38.

<sup>23</sup> H. Ohta, U. S. P. 1,801,364, April 21, 1931, to Asahi Glass Co., Ltd.; *Chem. Abs.*, 1931, 25, 3502. French P. 638,197, 1924; *Chem. Abs.*, 1928, 23, 293.

<sup>24</sup> W. H. Wright, U. S. P. 1,833,810, Nov. 24, 1931, to Schenectady Varnish Co.; *Chem. Abs.*, 1932, 26, 1143.

<sup>25</sup> S. Mizushima, *Researches Electrotech. Lab. Tokyo*, 1928, 221; *Chem. Abs.*, 1928, 22, 2070.

colophony to 250-300°C. until the oil polymerized and all volatile matter had escaped. The resulting mass was dissolved in benzene to form the cement.<sup>26</sup> A coating for insulating-tapes was proposed by Clark and Ruscetta.<sup>27</sup> The mixture consisted of ester gum (32-48 parts), montan wax (40-50 parts) and castor oil (10-28 parts).

**Special Uses of Ester Gum Varnishes.** One example of a coating requiring special properties is an anti-fouling paint, intended to retard the accumulation of marine growth on material in contact with sea water. The use of such paints to prevent marine borers from attacking wood was studied by Gardner.<sup>28</sup> Paints consisting of ester gum varnishes mixed with compounds of mercury or with cupric cyanide accomplished this special purpose. In further work, Gardner noted that certain white paints obtained from a benzol solution of ester gum were resistant to marine growths. An anti-fouling paint was prepared as follows: 650 pounds of ester gum were dissolved in 77 gallons of benzol, 10 gallons of spar varnish, 10 gallons of pine oil, a toxic substance and zinc oxide or Titanox were added and the mixture ground. After grinding, 48 gallons of benzol rubber solution were incorporated.<sup>29</sup> Ellis<sup>30</sup> employed rosin esters in coating compositions intended for application to concrete surfaces.

Ester gum mixed with tung oil, linseed oil, cobalt resinate, turpentine and pigments yields a composition that gives a flat finish to oilcloth.<sup>31</sup> A varnish, proposed for tin cans, is prepared from rosin, vegetable oil, a lead-free drier, glycerol, zinc and zinc oxide. The final product is applied to the interior of the can and baked at a high temperature. Since this coating contains no metals yielding colored sulphides, cans coated with it may be used for vegetables and fruits containing sulphur.<sup>32</sup> A varnish containing aluminum or brass powder in an ester gum vehicle was utilized by Bauer<sup>33</sup> to coat metal surfaces. After the coating has been applied, the metal is heated until the agglutinant begins to harden. The material is then subjected to pressure rolls to force the coating into the pores and inequalities of the surface. Finally, the varnish is baked until hard.

**Modification of Ester Gum Varnishes.** The incorporation of other substances with ester gum in varnishes is undertaken with the idea of changing in some way the characteristics of the final product. Mixing of other resins with ester gum during the preparation of a varnish yields a coating possessing some of the characteristics of each resin.<sup>34</sup> The film resulting from ester gum varnishes is hardened by adding a small amount of an oil-soluble phenol resin.<sup>35</sup> One method of incorporation is as follows: 15 kg. of Albertol 209L are mixed slowly with 20 kg. of varnish oil at 150°C. The temperature is raised to 260°C. and kept there until a specimen remains clear when diluted with an equal volume of thinner. After the addition of 100 kg. of heat-treated linseed oil, the temperature is maintained at 200°C. during the incorporation of ester gum (150 kg.) and then raised to 300°C. until the mixture is homogeneous. When the melt has cooled to 220°C. driers and thinners are added.

Gardner<sup>36</sup> heated a mixture of Aroclors with ester gum to produce a resinous

<sup>26</sup> German P. 525,483, 1928, to Siemens-Schuckertwerke A.-G.; *Chem. Abs.*, 1931, 25, 4072.

<sup>27</sup> F. M. Clark and R. A. Ruscetta, British P. 389,816, 1933, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 5446.

<sup>28</sup> H. A. Gardner, *Circ., U. S. Paint Mfrs. Assoc.*, 1923, 176, 207; *Chem. Abs.*, 1923, 17, 2511.

<sup>29</sup> H. A. Gardner, U. S. P. 1,493,930, May 13, 1924; *Chem. Abs.*, 1924, 18, 2257.

<sup>30</sup> Carleton Ellis, U. S. P. 1,189,550 and 1,189,551, July 4, 1916; *Chem. Abs.*, 1916, 10, 2136.

<sup>31</sup> E. E. Wallen, British P. 217,255, 1923; *Chem. Abs.*, 1925, 19, 409.

<sup>32</sup> R. H. Lueck, U. S. P. 1,667,212, Apr. 24, 1928, to the U. S. Public; *Chem. Abs.*, 1928, 22, 2071.

<sup>33</sup> W. Bauer, U. S. P. 1,823,869, Sept. 15, 1931; *Chem. Abs.*, 1932, 26, 76. British P. 331,550, 1929; *Chem. Abs.*, 1931, 25, 223.

<sup>34</sup> Ester-gum-modified phenol resins are discussed in Chapter 19. For alkyd resins in modified form, see Chapter 43. Maleic anhydride-ester gum resins are treated in Chapter 40.

<sup>35</sup> A. Nauroy, *Peintures, pigments, vernis*, 1930, 7, 1214, 1262; *Chem. Abs.*, 1931, 25, 2863.

<sup>36</sup> H. A. Gardner, British P. 351,637, 1930; *Brit. Chem. Abs. B*, 1931, 853. See Chapter 56 for other mixtures of Aroclors.

composition for oil varnishes or for nitrocellulose lacquers. A varnish may be prepared which has as a base a mixture of polystyrene with methyl tetrahydroabietate.<sup>37</sup> The inclusion of chloronaphthalenes, e.g., Halowax, in ester gum-tung oil varnish is said to improve its waterproofing characteristics.<sup>38</sup> According to Asser<sup>39</sup> the addition of a mixture of equal parts of phenol-formaldehyde and cresol-formaldehyde resin to ester gum raised its softening point from 68° to 110°C. The proportions used were 1 part of the phenol-resin mixture to 4.5 parts of melted ester gum fused at 150°C. until the melting point of the resulting resin is constant. It is reported that ethyl abietate when added to ester gum-tung oil varnishes improves the weathering properties of the final film but at the same time retards the rate of drying.<sup>40</sup>

Small amounts of antioxidants have been found to improve the quality of ester gum varnish films. For instance, Gardner and Sward<sup>41</sup> report that 0.1 per

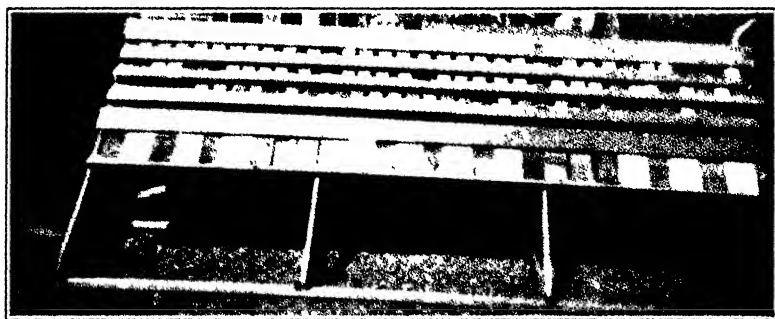


FIG. 123.—Testing Rack on Roof of Author's Laboratory for Exposure Tests on Synthetic Resin Coatings.

cent of sulphur introduced into an ester gum varnish improves its durability. Increasing the amount of sulphur to 0.5 per cent produced harmful effects. Various compounds said to give an anti-aging effect in ester gum-drying oil varnishes include trihydrophenol, catechol, dimethyl ether of pyrogallol or guaiacol, diphenylguanidine and di-*o*-tolyl-guanidine.<sup>42</sup>

Although varnishes form the principal outlet for drying oil-ester gum mixtures small amounts have found use in other ways. Ester gum cooked in tung oil has been mixed with the customary ingredients and coated onto a felt base to make a floor covering.<sup>43</sup> A binder containing ester gum (50 parts), cumarone resin (50 parts), dibutyl tartrate (35 parts) and polymerized linseed oil (10 parts) has been suggested for cementing wood flour and cork in the manufacture of linoleum.<sup>44</sup>

Core oil (for foundry work) is sometimes comprised of rosin, linseed oil and thinner. McArdle<sup>45</sup> has employed ester gum, corn or soya bean oil and thinner to make a similar product.

<sup>37</sup> British P. 375,320, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 807.

<sup>38</sup> British P. 342,737, to Bakelite Corp.; *Brit. Chem. Abs.* B, 1931, 452.

<sup>39</sup> E. Asser, U. S. P. 1,969,292, Aug. 7, 1934; *Chem. Abs.*, 1934, 28, 6329.

<sup>40</sup> *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1929, 356, 900; *Brit. Chem. Abs.* B, 1930, 68.

<sup>41</sup> H. A. Gardner and G. G. Sward, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1932, 410, 129; *Brit. Chem. Abs.* B, 1933, 77.

<sup>42</sup> British P. 358,472, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 4969.

<sup>43</sup> D. Finley, U. S. P. 1,802,009, Apr. 21, 1931; *Chem. Abs.*, 1931, 25, 3504.

<sup>44</sup> J. T. Baldwin, U. S. P. 1,793,667, Feb. 14, 1931, to Sandura Co.; *Chem. Abs.*, 1931, 25, 2313.

U. S. P. 1,856,369 and 1,856,370, May 3, 1932; *Chem. Abs.*, 1932, 26, 3686.

<sup>45</sup> E. H. McArdle, U. S. P. 1,822,411, Sept. 8, 1931, to A. Klipstein & Co.; *Brit. Chem. Abs.* B, 1932, 649.

An aqueous coating composition containing ester gum was proposed by Holman and Hooppaw.<sup>46</sup> The other ingredients in this paint were magnesium oxide, magnesium chloride, magnesium sulphate, pigments, tung oil and petroleum spirits.

#### RESIN ESTERS IN CELLULOSE LACQUERS

Cellulose lacquers have been utilized in situations where speed of application and drying are of importance. The oil-soluble resins are still widely used when spraying or dipping are impractical and drying-time is not of importance. In addition, resin varnishes enjoy another advantage in that they are generally cheaper. The characteristics of a nitrocellulose lacquer may be changed by the addition of a resin. The incorporation of resins in a lacquer increases the content of solids and improves the adhesion and gloss. Of the resins employed ester gum is one of the more popular because of its availability and because it is soluble in many lacquer solvents.

The properties required for ester gum to be incorporated in lacquers are approximately the same as those desired for oil varnishes. The resin should possess an acid number below 20 and a pale color. In addition, the ester should not contain any free glycerol, since the latter has a deleterious effect on the final film.

In preparing a nitrocellulose lacquer, the ester gum is first dissolved in a compatible diluent before it is incorporated in the lacquer. Benzene, toluene, ethyl acetate and butyl acetate are generally employed for this purpose. When the addition of an ester to a lacquer is being considered every ingredient that is to be incorporated must be studied. The quality of the nitrocellulose, the type of plasticizer, the character of the solvent and diluents determine as much as the ester the properties of the final coating. For instance, ester gum is not soluble in diacetone alcohol, ethyl lactate, Cellosolve or Cellosolve acetate.<sup>47</sup>

One nitrocellulose lacquer containing ester gum is described by Bogin.<sup>48</sup> The lacquer contains 0.5-1.0 pound of nitrocellulose and an equal weight of ester gum in 1 gallon of a solvent mixture comprising 10 per cent of a nitrocellulose solvent (b.p. 140-180°C), 10 per cent of cyclohexanol, 30 per cent ethyl acetate and 50 per cent of mixed benzene and toluene. In determining the optimum proportion of rosin-glycerol ester to solvent, Mowen<sup>49</sup> concluded that 16 pounds to 1 gallon of hydrocarbon (toluene) solvent give the best product. However, a proportion as high as 20 pounds of resin to 1 gallon of liquid is feasible. Symons<sup>50</sup> reports that the best ratio is equal parts of ester gum and nitrocellulose plus plasticizer amounting to 30 per cent of dry weight of the nitrocellulose.

Mention has been made that free glycerol in the rosin ester has a harmful effect on the final film. One method recommended to overcome this difficulty is to esterify with polyglycerol. The presence of this reagent is said to have no harmful effect on the final film.<sup>51</sup> It has been reported that the use of glyceryl diabietate in place of the triabietate in lacquers gives a film of good hardness and toughness.<sup>52</sup> The mixed esters of polyhydric aliphatic alcohols with higher fatty acids and resin acids have been employed as softening agents in oil-free cellulose ester or ether lacquers.<sup>53</sup>

Of the other esters of abietic acid, ethyl abietate appears to have a large field

<sup>46</sup> C. H. Holman and O. W. Hooppaw, U. S. P. 1,734,130, Nov. 5, 1929; *Chem. Abs.*, 1930, 24, 516.

<sup>47</sup> H. E. Hofmann, *Ind. Eng. Chem.*, 1931, 23, 127.

<sup>48</sup> C. Bogin, U. S. P. 1,651,578, Dec. 6, 1927, to Commercial Solvents Corp.; *Chem. Abs.*, 1928, 22, 878.

<sup>49</sup> P. M. Mowen, *Paint, Oil, Chem. Rev.*, 1928, 85 (19), 10.

<sup>50</sup> P. S. Symons, *Paint, Varnish Prod. Mgr.*, 1931, 5 (4), 8.

<sup>51</sup> A. Fairbourne, G. P. Gibson and D. W. Stephens, *J.S.C.I.*, 1930, 49, 1069.

<sup>52</sup> H. Wolf and H. Zellner, German P. 502,263, 1926; *Chem. Abs.*, 1930, 24, 4944.

<sup>53</sup> German P. 506,306, 1929, to Firma L. Blumer; *Chem. Abs.*, 1923, 27, 1219.

of usefulness. It is said to act both as a resin and plasticizer. This would be an advantage because the necessity of adjusting the solvents and diluents to both resin and plasticizers would be eliminated.<sup>54</sup> A similar behavior was observed also by Johnston.<sup>55</sup> He found that ethyl abietate dissolves ester gum, elemi, mastic and rosin. If desired, however, it can be used in conjunction with other plasticizers. The films resulting from the addition of this ester to lacquers are said to be less tacky than those containing ester gum. The proportions recommended are 10 parts of half-second nitrocellulose to 26 parts of ethyl abietate. Employing the same ingredients, Bent<sup>56</sup> noticed that the films dried quickly and were durable. Kesler<sup>57</sup> reported that many esters of abietic acid resemble ethyl abietate in their combined plasticizer and resin effect. These resins could be substituted for plasticizers such as dibutyl phthalate.

Some esters of abietic acid other than those previously mentioned have been suggested for addition to cellulose lacquers. For instance, the hydroxyalkyl esters, which are made with alkylene oxides and abietic acid, can be used as softening agents for lacquers.<sup>58</sup> Chlorinated rosin is also reported to be a good resin for adding to nitrocellulose coatings.<sup>59</sup> In some cases improved films result when another resin is employed in addition to ester gum in nitrocellulose lacquers. Dammar added to an ester-gum-containing lacquer seems to increase the adhesiveness of the coating and to decrease chalking. A composition of this sort proposed by Gilbert<sup>60</sup> contains the following substances:

	Per Cent by Weight
Low-viscosity nitrocellulose . . .	10.
Dammar resin . . . . .	2 5
Ester gum . . . . .	2.5
Castor oil . . . . .	3 0
Dibutyl phthalate . . . . .	3.
Antimony oxide . . . . .	15.
Solvents and diluents . . . . .	64.

A mixture of ester gum, 1.5-3 parts and a cumarone-indene resin, 1 part, has been recommended for addition to nitrocellulose to yield a non-blushing film.<sup>61</sup>

Gardner<sup>62</sup> found that methyl or butyl esters of shellac give good elasticity and gloss to the lacquer film. These esters act not only as resins but may replace also the plasticizers in cellulose ester compositions. The esterification of Catavia resin (a balsam from Panama) gives a product that possesses possibilities as a varnish resin.<sup>63</sup>

Barrett<sup>64</sup> proposed the inclusion of hydroquinone to inhibit atmospheric oxidation of nitrocellulose films. Phosphorescent coatings can be produced by grinding luminous salts with rosin esters. This mixture is then incorporated with a plasticized cellulose lacquer to give the final product.<sup>65</sup>

Of the cellulose esters, the nitrate has the largest use as a lacquer constituent.

<sup>54</sup> T. H. Barry, "Natural Varnish Resins," E. Benn, Ltd., London, 1932.

<sup>55</sup> A. C. Johnston, *Ind. Eng. Chem.*, 1929, 21, 688. See also *Melland Textile Monthly*, 1932, 4, 135.

<sup>56</sup> L. N. Bent, U. S. P. 1,839,529, Jan. 5, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1932, 26, 1460.

<sup>57</sup> C. C. Kesler, A. Lowy and W. F. Faragher, *J.A.C.S.*, 1927, 49, 2898.

<sup>58</sup> O. Schmidt and E. Meyer, German P. 561,626, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1219. British P. 328,190, 1928; *Chem. Abs.*, 1930, 24, 5518.

<sup>59</sup> L. W. Eberlin and L. W. Blanchard, U. S. P. 1,899,186, Feb. 28, 1933, to Eastman Kodak Co.; *Chem. Abs.*, 1933, 27, 2094.

<sup>60</sup> J. W. Gilbert, U. S. P. 1,914,563, June 20, 1933, to E. I. du Pont de Nemours and Co.; *Chem. Abs.*, 1933, 27, 4427.

<sup>61</sup> A. Rogers, U. S. P. 1,884,255, Oct. 25, 1932, to Barrett Co.; *Chem. Abs.*, 1933, 27, 1219.

<sup>62</sup> W. H. Gardner, U. S. P. 1,910,100, May 23, 1933; *Chem. Abs.*, 1933, 27, 4103.

<sup>63</sup> L. P. Hart, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1931, 377, 131; *Brit. Chem. Abs. B*, 1931, 451.

<sup>64</sup> G. R. Barrett, U. S. P. 1,720,992, July 16, 1929, to Merrimac Chemical Co.; *Chem. Abs.*, 1929, 23, 4356.

<sup>65</sup> J. A. Beavis, British P. 299,228, 1928; *Brit. Chem. Abs. B*, 1929, 64.

Because of its inflammability and tendency to hydrolyze, attempts have been made to replace it with other esters or ethers. Dreyfus<sup>66</sup> has reported that ester gum may be used with low-viscosity methyl, ethyl and benzyl cellulose. One such lacquer contained the following ingredients; ethyl cellulose (10 parts), ester gum (5 parts), toluene (90 parts), liquid paraffin (1.5 parts) and dibutyl phthalate (0.5 part).<sup>67</sup>

Ester gum has been incorporated in lacquers which are aqueous emulsions of cellulose esters. An example of one such lacquer is as follows: 0.25 part of sodium oleate in 40 parts of water are added to a solution containing nitrocellulose (12 parts), ester gum (4 parts), tricresyl phosphate (6 parts), chrome yellow (8 parts) and cyclohexanone (60 parts). The compositions are said to dry to hard transparent films.<sup>68</sup> Aqueous dispersions of ester gum are obtained by adjusting and holding the hydrogen ion concentration of the system within certain limits. This may be accomplished with colloidal clay or bentonite.<sup>69</sup>

Compositions containing rosin esters and a cellulose ester have been proposed for purposes other than lacquer coatings. Ethyl abietate has been suggested as an agent for replacing linseed oil in coating compositions used in the manufacture of floor covering. The resulting linoleum is said to be flexible and resilient. Objectionable odors which develop from plasticizing-oil are eliminated.<sup>70</sup> An illustration of a recommended composition follows:

Soluble nitrocellulose	..	28	parts	by	weight.
Ethyl abietate		31	"	"	"
Tricresyl phosphate		7	"	"	"
Wood flour		34	"	"	"

In another proposal a mixture of ester gum, benzylcellulose, dicresylm and cork dust is utilized to prepare a flooring composition.<sup>71</sup>

Thin waterproof sheets are prepared from a solution containing nitrocellulose, ester gum, dibutyl phthalate and paraffin. The solution is dried at a temperature higher than the melting point of the wax.<sup>72</sup> A homogeneous smokeless powder was obtained by Norton<sup>73</sup> from nitrocellulose (60-90 parts), ethyl, phenol or benzyl abietate (5-25 parts) and nitroglycerine (5-30 parts). Ester gum has been included in a nitrocellulose bonding material for making floor tile of finely divided cork.<sup>74</sup>

#### NITROCELLULOSE-ESTER GUM-OIL COMPOSITIONS

The modification of cellulose lacquers by the addition of drying oils has been suggested in attempts to obtain improved coatings. Of course, for such incorporation, care must be taken not only to obtain a homogeneous solution of the various ingredients (apart from pigments) but that such a solution dries evenly in films without separation of the cellulose ester, an occurrence which would result in a slow-drying gel.

Studying the addition of tung oil to ester gum-nitrocellulose lacquers, Flood, Booth and Beisler<sup>75</sup> concluded that it is possible to obtain tough water-resistant

<sup>66</sup> C. Dreyfus, British P. 309,951, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 739.

<sup>67</sup> British P. 363,333, 1930, to Imperial Chem. Ind., Ltd. See also British P. 309,951, 1929.

<sup>68</sup> W. J. Jenkins, British P. 310,062, 1929, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.* B, 1929.

483. G. P. Davies and W. J. Jenkins, British P. 328,657, 1930; *Chem. Abs.*, 1930, 24, 5517.

<sup>69</sup> French P. 655,355, 1928, to Flintkote Co.; *Chem. Abs.*, 1929, 23, 4061.

<sup>70</sup> J. H. Rile, U. S. P. 1,890,128, Dec. 6, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 1734.

British P. 308,524, 1928; *Chem. Abs.*, 1930, 24, 238.

<sup>71</sup> A. C. Hetherington and S. S. Sun, U. S. P. 1,970,090, Aug. 14, 1934, to Imperial Chem. Ind. Ltd.; *Chem. Abs.*, 1934, 28, 6271. British P. 381,590, 1932; *Chem. Abs.*, 1933, 27, 5535.

<sup>72</sup> French P. 647,330, 1927, to Du Pont Cellophane Co., Inc.; *Chem. Abs.*, 1929, 23, 2542.

<sup>73</sup> S. G. Norton, U. S. P. 1,788,438, Jan. 13, 1931, to Hercules Powder Co.; *Chem. Abs.*, 1931, 25, 1086.

<sup>74</sup> J. E. Graham, U. S. P. 1,876,289, Sept. 6, 1932, to Bird & Son, Inc.; *Chem. Abs.*, 1933, 27, 176.

<sup>75</sup> W. E. Flood, D. C. Booth and W. H. Beisler, *Ind. Eng. Chem.*, 1928, 20, 609.



films from these compositions. These workers found that the addition of raw tung oil to the lacquer containing ester gums yielded coatings that gave opaque films of low tensile strength. The use of bodied tung oil produced better results but the final films were red in color. By heating the ester gum with tung oil and then adding to nitrocellulose, the resulting composition possessed the desired properties. Ester gum, tung oil and glycerol were refluxed at 275°C for 2 hours and steam passed through the mixture 45 minutes at 180°C. As much as 30 per cent tung oil was incorporated with the rosin ester. This resin was dissolved in a thinner and added to the nitrocellulose solution. One composition contained the following substances (by weight):

Dry nitrocellulose	19.2 parts
Ethanol	8.2 "
Amyl acetate	30.0 "
Benzene	13.5 "
Ester gum-tung oil resin	5.7 "
Ethyl acetate	6.8 "
Diacetone alcohol	3.0 "
Xylene	13.5 "

Exposure tests on wooden panels indicated that the presence of tung oil increases the durability of the films. From his experimental work, Kolke<sup>76</sup> found that the combination of a rosin ester-tung oil varnish with a butyl acetate solution of nitro-cotton yielded a good lacquer.

A method of preparing an ester gum-tung oil-nitrocellulose composition is described by Swartz.<sup>77</sup> Fifty pounds of ester and 15 gallons of oil are heated to 200°C, 4 pounds of litharge added and the temperature raised to 280°C. At 290°C 50 pounds more of ester gum are added. Manganese resinate is incorporated at 260°C. and toluene at 175°C. This composition is added to an equal volume of a solution made from 2 pounds of dry, half-second R. S. Cotton, 1 gallon of butyl acetate and 21 per cent of plasticizer. The final product may be applied as a spray or thinned with toluol, butanol or butyl propionate for brushing. When sprayed onto wood the coating will dry to touch in 15 minutes and hard enough to handle in 2 hours.

In some instances linseed oil has been employed in this type of coating but for most purposes tung oil has been found to give the best results. A flat varnish containing linseed oil was prepared by Burgemeister<sup>78</sup> by melting the ingredients together at 280-300°C. As an example, ester gum (250 parts), linseed oil (500 parts) and ethyl cellulose (250 parts) were heated until oil and resin dissolved. Jenkins<sup>79</sup> added  $\beta$ -hydroxy methyl propionate to a linseed oil lacquer. One such composition contained nitrocellulose (12 parts), butyl propionate (5 parts),  $\beta$ -hydroxy methyl propionate (10 parts), butyl alcohol (25 parts), ester gum (10 parts), linseed oil (10 parts), tricresyl phosphate (3 parts), xylene (20 parts) and turpentine (5 parts).

An oxidized ester gum-linseed oil mixture was proposed by Bonney and Egge<sup>80</sup> for addition to lacquers. The mixture consisted of linseed oil (3 parts) and ester gum (1 part). This was heated to 115°C. until the resin dissolved; then a drier was added. The mass was aerated for 25-30 hours at 80°C. until it became viscous. The unoxidized constituents of the batch were extracted by petroleum naphtha. Thirty parts of the product were mixed with cellulose nitrate (10 parts) and solvent (60 parts) to give clear protective coatings. Another composition consists of linoloxyn, ester gum, cellulose acetate, tricresyl phosphate, castor oil, sol-

<sup>76</sup> F. Kolke, *Farben-Ztg.*, 1928, **33**, 861.

<sup>77</sup> M. D. Swartz, *Paint, Oil, Chem. Rev.*, 1926, **82** (20) 12.

<sup>78</sup> K. Burgemeister, German P. 523,300, 1928; *Chem. Abs.*, 1931, **25** 3502.

<sup>79</sup> W. J. Jenkins, British P. 307,528, 1927, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1929 365.

<sup>80</sup> R. D. Bonney and W. S. Egge, U. S. P. 1,968,243, July 31, 1934, to Congoleum-Naun, Inc.; *Chem. Abs.*, 1934, **28**, 6002.

vents and diluents.<sup>61</sup> Ellis<sup>62</sup> employed a destructively-distilled castor-oil condensation product for incorporation into pyroxylin lacquers containing ester gum.

Rosin ester, cellulose derivatives and oil have been added to plastic compositions. Griffiths<sup>63</sup> prepared such a combination from nitrocellulose (15-20 parts), ester gum (5-9 parts), castor oil (1-5 parts), solvent (66-79 parts) and wood flour (15-30) parts. Another plastic composition is made from nitrocellulose, bodied linseed oil, ester gum, solvents and powdered slate.<sup>64</sup>

A thermoplastic composition, produced from a mixture of glycerol, rosin, tung oil and stearin has been proposed by Hadley.<sup>65</sup> The mixture is heated until the oil is polymerized, the rosin esterified and the volatile matter driven off. The resulting composition is used with mica to form electrical insulators. A composition containing ester gum, nitrocellulose, castor oil and lampblack has been suggested as a printing ink.<sup>66</sup>

**Properties of Nitrocellulose-Resin Films.** As was already stated, the incorporation of esters with lacquers alters the characteristics of the coating composition. Effect of esters upon the time of drying and method of application has been mentioned previously. The largest changes in the final coating are probably those with respect to adhesiveness and gloss.

Tests on the adhesiveness of nitrocellulose films were carried out by Gardner and Van Heuckeroth.<sup>67</sup> A number of lacquers and resin-lacquer compositions were coated onto different surfaces. After drying, the coating was stripped off.<sup>68</sup> The load (in grams) required to remove the film from the material is taken as a measure of the adhesiveness of the film. In Table 40 are given the results of a lacquer containing 9 per cent of dibutyl phthalate and one consisting of 100 parts of cotton base<sup>69</sup> and 25 parts of ester gum dissolved in toluene (25 parts), toluene (50 parts) and dibutyl phthalate (10 parts), after each had dried 6 days.

TABLE 40.—Adherence of Lacquers to Various Surfaces.

Material	Galvanized	Black	Glass	Wood	Tin	Aluminum
	Iron	Iron				
Lacquer . . . . .	280	20	320	460	0	0
Ester gum-lacquer . . .	600	200	400	480	100	20

Results are expressed as load in grams required to strip coating from material.

In testing lacquers, Merz<sup>70</sup> varied the proportion of ester gum from 0 to 100 per cent (based on total solids). As the percentage of rosin ester increased the film became more brittle, but up to 70 per cent ester gum had comparatively slight effect on the durability (by accelerated methods). However, Duncan, Wiggam and Davey<sup>71</sup> concluded from their work on light-absorption by lacquer films that ester gum was affected by ultraviolet light. This is not a large factor however in lacquers containing pigments because these solids protect the film by rendering it opaque.

After studying color, gloss, binding power, elasticity and durability of lacquers

<sup>61</sup> British P. 307,361, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 780. Blown oils and solid waxes are included in other compositions. See British P. 419,688, 1933, to Sylvania Industrial Corp.; *Brit. Chem. Abs.* B, 1935, 320.

<sup>62</sup> C. T. Ellis, U. S. P. 1,934,261, Nov. 7, 1933, to Sherwin-Williams Co.; *Chem. Abs.*, 1934, 28, 663.

<sup>63</sup> M. E. Griffiths, U. S. P. 1,838,618, Dec. 20, 1931, to A. S. Boyle Co.; *Chem. Abs.*, 1932, 26, 1460.

<sup>64</sup> German P. 514,640, 1925, to I. G. Farbenind. A.-G.

<sup>65</sup> G. F. Hadley, U. S. P. 1,948,756, Feb. 27, 1934, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1934, 28, 2812.

<sup>66</sup> French P. 698,639, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3184.

<sup>67</sup> H. A. Gardner and A. W. Van Heuckeroth, *Ind. Eng. Chem.*, 1928, 20, 600.

<sup>68</sup> See Chapter 70 for details of test.

<sup>69</sup> The cotton base contained 32 ounces of half-second nitrocellulose in 1 gallon of butyl acetate.

<sup>70</sup> O. Merz, *Farben-Ztg.*, 1930, 36, 316, 3627; *Brit. Chem. Abs.* B, 1931, 72.

<sup>71</sup> D. C. Duncan, D. R. Wiggam and W. P. Davey, *Ind. Eng. Chem.*, 1931, 23, 904.

containing various resins, Toeldte<sup>92</sup> decided that ester gum was among the best for incorporation with nitrocellulose. Experiments on the tensile strength of nitrocellulose films by Jones and Miles<sup>93</sup> showed that lacquers containing ester gums had high tensile strength. These workers found that the properties of the nitrocellulose solvents and plasticizers employed affected the characteristics so much that these as well as the ester gum have to be considered in judging a lacquer.

#### SOLUTIONS OF RESIN ESTERS

Solutions of esters without drying oils have been proposed for use as coating compositions. If the solvent is volatile, waterproof coatings are quickly formed. These compositions of course do not exhibit all the desirable properties of an oil varnish. However, they are practical for certain purposes. The use to which the coating is to be put generally determines the solvent employed. Acetone is one solvent that has been suggested. Woodford<sup>94</sup> dissolved ester gum (1 part) in acetone (3 parts) to produce a liquid that would adhere well to paraffin paper and dry in 10 seconds. A solution comprising equal parts of ester gum, rosin and acetone was used to size and waterproof fabrics.<sup>95</sup> To make a photographic film non-static, Seel<sup>96</sup> coated it with a 3 per cent solution of ester gum in acetone. Esters of 9,11-octadecadiene-1-carboxylic acid with glycerol were used by Scheiber<sup>97</sup> in conjunction with ester gum to prepare vehicles for printing inks. A bronze printing ink, which contained finely divided metal, ester gum and terpineol was made by McElroy and Clarke.<sup>98</sup> A turpentine solution of ester gum was included in a metal polish by Jones and Harding.<sup>99</sup> The polish was said to leave a protective film not easily removed by rubbing.

A carbon paper is obtained by coating paper with a composition consisting of resin esters and coloring matter dissolved in a volatile liquid.<sup>100</sup> The resinates of amino alcohols, employed with volatile solvents, are suggested as sizing for textiles or cellulose pulps.<sup>101</sup> A solution of an ester gum has been used for sealing the edges of safety glass. The solvent chosen should also soften the edges of the central layer.<sup>102</sup>

#### MIXTURES OF ESTER GUM AND RUBBER

Ester gum has been mixed with rubber to prepare materials whose properties and uses depend upon relative proportions of ingredients and fillers. A plastic adhesive rubber composition is produced by heating ester gum (10 parts) and vulcanized rubber (4-15 parts) for 6 hours in an autoclave at 175°C.<sup>103</sup> Ester gum dispersions in reclaimed rubber (100:50-200) can be diluted with a solvent (e.g.,

<sup>92</sup> W. Toeldte, *Farben-Ztg.*, 1931, 37, 448; *Chem. Abs.*, 1932, 26, 1807. See also H. Wolff and W. Toeldte, *Farben-Ztg.*, 1929, 35, 2311; *Brit. Chem. Abs. B.*, 1929, 1046.

<sup>93</sup> G. G. Jones and F. D. Miles, *J.S.C.I.*, 1933, 52, 251T. See also Wachholtz, *Fachauschuss Anstrichtechnik Ver. Deut. Ing.*, 1929, 3, 34; *Chem. Abs.*, 1930, 24, 4174.

<sup>94</sup> W. H. Woodford, U. S. P. 1,733,177, Oct. 29, 1929, to Remington Arms Co.; *Chem. Abs.*, 1930, 24, 515.

<sup>95</sup> H. E. Butterfield, British P. 163,174, 1920; *J.S.C.I.*, 1921, 40, 732A.

<sup>96</sup> P. C. Seel, U. S. P. 1,687,042, Oct. 9, 1928, to Eastman Kodak Co.; *Chem. Abs.*, 1928, 22, 4394.

<sup>97</sup> J. Scheiber, German P. 522,480, 1931; *Chem. Abs.*, 1931, 25, 3184.

<sup>98</sup> W. J. McElroy and J. Clarke, U. S. P. 1,489,356, Apr. 8, 1924; *Chem. Abs.*, 1924, 18, 1915. British P. 197,916, 1923, to Alchemic Gold Co.; *J.S.C.I.*, 1923, 42, 1234A.

<sup>99</sup> L. S. Jones and H. J. Harding, British P. 198,807, 1922; *Chem. Abs.*, 1924, 18, 312.

<sup>100</sup> British P. 307,435, 1928, to Firm of G. Wagner; *Chem. Abs.*, 1929, 23, 5285. British P. 324,359, 1928; *Chem. Abs.*, 1930, 24, 3903.

<sup>101</sup> A. I. Kusnetsov, French P. 704,431, 1930; *Chem. Abs.*, 1932, 26, 1455.

<sup>102</sup> J. Wilson, British P. 326,359, 1928, to Triplex Safety Glass Co., Ltd.; *Chem. Abs.*, 1930, 24, 4369.

<sup>103</sup> W. L. Semon, U. S. P. 1,892,167, Dec. 12, 1932, to B. F. Goodrich Co.; *Brit. Chem. Abs. B.*, 1933, 757.

gasoline, carbon tetrachloride) to obtain an adhesive.<sup>104</sup> A rubber composition for shoe soles was made from esters of rosin, rubber, gasoline, fibrous material, sulphur, lampblack and resin emulsion.<sup>105</sup> The addition of 5-30 per cent ethyl abietate (as a plasticizer) to a mixture of gutta-percha and deproteinized rubber yields an insulating material that can be used for high-frequency cables.<sup>106</sup> Ethylene oxide-abietic ester has been employed with a butadiene polymerization product in the preparation of insulated cables.<sup>107</sup>

A cement consisting of solid chlorinated naphthalene (Halowax), ester gum and rubber latex has been suggested as a bonding agent for glass, metal and wood.<sup>108</sup> The cement is fused and applied to articles that have been heated to 110°C.

The use of a synthetic resin in chewing gum is of course contingent on the absence of any undesirable flavor. Weber<sup>109</sup> found that ester gum, after treatment with dry steam at 150°C. could be employed successfully for this purpose. One chewing gum proposed contained 25 pounds of chicla to 10 pounds of ester gum. A chicla substitute was prepared from natural rubber and the rosin esters of glycerol, glycol or naphthol.<sup>110</sup> A paraffin wax-rubber base mixed with ester gum gives a bland tasteless mass when heated to 145°C. The consistency of the chewing gum is controlled by the proportion of ester.<sup>111</sup> The benzyl ester of abietic acid, which is a resinous material softer than ester gum, was proposed for use in chewing gum and as a waterproofing agent for paper.<sup>112</sup>

#### ESTER GUM IN PAPER COATINGS

Among the numerous materials which have been proposed for impregnating paper for various reasons (waterproofing, preparing stencils, etc.), mixtures containing ester gum have found some use. For instance, a waterproofing composition was prepared by Pearsall<sup>113</sup> from petrolatum wax (15-95 parts) and ester gum (5-85 parts). The coating is non-tacky and will not stain white paper. It is said to be good for waterproofing fuses. Acoustic diaphragms, constructed of cloth or paper, are made air-impervious and water-repellant by a mixture composed of equal parts of tung oil and ester gum.<sup>114</sup> A composition, proposed for waterproofing paper, contains a cellulose ester, ester gum, wax, plasticizer and solvent.<sup>115</sup>

Certain esters have been included in coatings for application on thin tissue paper to make stencil sheets. One such mixture consists of mineral wax and a polyhydric ester of bleached montan wax. Another one was produced from cellulose esters, naphthenic acid glycerides and a heavy hydrocarbon oil.<sup>116</sup> A solution of ester gum, turpentine and castor oil was coated onto backing-sheets for duplicating-machine stencil sheets.<sup>117</sup> Decalcomania paper with a design thereon is provided with a coating containing nitrocellulose, ester gum, plasticizer and solvent.<sup>118</sup>

<sup>104</sup> W. F. Zimmerli and R. S. Havenhill, U. S. P. 1,892,123, Dec. 27, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 2001.

<sup>105</sup> S. I. Rivkin and I. A. Skorov, Russian P. 30,955, 1933; *Chem. Abs.*, 1934, 28, 3620.

<sup>106</sup> A. R. Kemp, British P. 404,027, 1932, to Electrical Resinous Products, Inc.; *Brit. Chem. Abs. B*, 1934, 207.

<sup>107</sup> British P. 332,891, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 955. For the addition of esters to butadiene polymerization products see Chapter 9.

<sup>108</sup> M. E. Delaney, U. S. P. 1,945,803, Feb. 6, 1934, to Halowax Corp.; *Chem. Abs.*, 1934, 28, 2481.

<sup>109</sup> H. M. Weber, U. S. P. 1,401,452, Dec. 27, 1921, to Ellis-Foster Co.

<sup>110</sup> W. O. Snelling, U. S. P. 1,430,036, Sept. 9, 1922; *Chem. Abs.*, 1922, 16, 4094.

<sup>111</sup> C. E. Dellenbarger, U. S. P. 1,786,831, Dec. 30, 1930, to P. Carpenter; *Brit. Chem. Abs. B*, 1931, 1026.

<sup>112</sup> F. D. Crane, U. S. P. 1,513,802, Nov. 4, 1924; *Chem. Abs.*, 1925, 19, 186.

<sup>113</sup> D. E. Pearsall, U. S. P. 1,968,807, Aug. 7, 1934, to Ensign-Bickford Co.; *Chem. Abs.*, 1934, 28, 6314.

<sup>114</sup> G. H. Burgman, U. S. P. 1,911,802, May 30, 1933, to G. J. Liebhich Co.; *Chem. Abs.*, 1933, 27, 4044.

<sup>115</sup> W. H. Church and K. E. Prindle, British P. 283,109, Jan. 3, 1927, to Du Pont Cellophane Co., Inc.; *Chem. Abs.*, 1928, 22, 3991.

<sup>116</sup> S. Horii, U. S. P. 1,792,095, Feb. 10, 1931; *Chem. Abs.*, 1931, 25, 1958. U. S. P. 1,885,261, Nov. 1, 1932; *Chem. Abs.*, 1933, 27, 1119.

<sup>117</sup> S. Horii, British P. 810,126, 1928; *Chem. Abs.*, 1930, 24, 699.

<sup>118</sup> R. Tuill, U. S. P. 1,826,228, Oct. 6, 1931, to Western Lithograph Co.; *Chem. Abs.*, 1932, 26, 569.

A fusible composition, which on heating is intended to be transferred from the original paper (dry transfer), was obtained by Lawrence<sup>119</sup> from a mixture of rosin ester, wax, castor oil, cadmium selenide and solvent. Another combination used for the same purpose is composed of ethyl cellulose, ethyl abietate, cumarone, gold bronze, the monoethyl ether of diethylene glycol (Carbitol) and castor oil.<sup>120</sup> Ethyl and butyl abietate have been mentioned as plasticizers for phenolic resinoids to be employed as cements in the making of laminated material from paper.<sup>121</sup>

#### MISCELLANEOUS USES OF ESTER GUM

Ester gum has been added to plastic compositions to replace more costly materials or to modify in some manner the properties of the product. Generally ester gum does not constitute a large percentage of the total mass. One such plastic composition proposed by Hull<sup>122</sup> contained casein (50 parts), furfural (5 parts), ester gum (5 parts), slate dust (40 parts). The mass was molded at 100°C. for 50 minutes under a pressure of 3 tons to the square inch. Another plastic mass includes ester gum and kieselguhr among its ingredients.<sup>123</sup> The esterification product of copal with polyhydroxy fatty acids has been suggested as a binding medium in the making of phonograph records.<sup>124</sup>

The addition of ester gum to a composition containing camphor and nitrocellulose lowers the modulus of elasticity of the resulting celluloid.<sup>125</sup> A mixture of this type containing a resin ester has been employed as a shoe-upper stiffener (e.g., box toes).<sup>126</sup>

The esterification of rosin and phenol in the presence of mineral acids yields a resin insoluble in water. It is rendered soluble by sulphonation, the resulting product being employed as a tanning agent.<sup>127</sup>

Esters of abietic acid and montan wax may be used as emulsifying, cleansing and wetting agents. Triethanolamine abietate has been proposed as emulsifier in the preparation of a pyrethrum emulsion.<sup>128</sup> The acids of crude or treated montan wax were esterified with aliphatic or aralkyl alcohols to give materials which may be utilized as wetting, emulsifying, cleansing and sizing agents.<sup>129</sup> A mixture of hexamethylenetetramine (1-25 per cent) and ethyl abietate (75-99 per cent) was employed as a soldering flux by McBride.<sup>130</sup> Heptaldehyde and undecylenic acid have been obtained from a mixture of raw castor oil and ester gum destructively distilled *in vacuo* at 300-340°C.<sup>131</sup>

<sup>119</sup> W. S. Lawrence, U. S. P. 1,941,697, Jan. 2, 1934, to Kaumagraph Co.; *Brit. Chem. Abs. B*, 1934, 924.

<sup>120</sup> W. S. Lawrence, U. S. P. 1,899,420, Feb. 28, 1933, to Kaumagraph Co.; *Chem. Abs.*, 1933, 27, 3048; *British P.* 338,611, 1929.

<sup>121</sup> French P. 685,801, 1930, to Bakelite Corp.; *Chem. Zentr.*, 1931, 1, 1530. *British P.* 343,572, 1929. *Brit. Chem. Abs. B*, 1931, 482.

<sup>122</sup> S. M. Hull, U. S. P. 1,711,025, Apr. 30, 1929, to Western Electric Co.; *Chem. Abs.*, 1929, 23, 3060.

<sup>123</sup> French P. 731,431, 1932, to I. G. Farbenind. A.-G.

<sup>124</sup> W. Dux, *British P.* 350,764, 1929; *Chem. Abs.*, 1932, 26, 3124. See also German P. 551,093, 1929. *Chem. Abs.*, 1932, 26, 4487.

<sup>125</sup> P. Heymans and G. Calingaut, *Ind. Eng. Chem.*, 1924, 16, 939.

<sup>126</sup> D. B. Macdonald, *British P.* 397,141, 1933, to British United Shoe Machinery Co. Ltd.; *Chem. Abs.*, 1934, 28, 1490.

<sup>127</sup> A. Doser and A. Thaus, U. S. P. 1,788,371 and 1,788,372, Jan. 13, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1109. *British P.* 302,938, 1928; *Brit. Chem. Abs. B*, 1930, 941. *British P.* 321,190, 1928; *Brit. Chem. Abs. B*, 1930, 410.

<sup>128</sup> German P. 525,821, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4654.

<sup>129</sup> *British P.* 371,822, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3045.

<sup>130</sup> F. D. McBride, U. S. P. 1,929,895, Oct. 10, 1934, to Berry Solder Co.; *Chem. Abs.*, 1934, 28, 94.

<sup>131</sup> H. A. Bruson and J. D. Robinson, U. S. P. 1,889,348, Nov. 29, 1932, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1933, 27, 1365.

## *MEMORANDA*

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# THE CHEMISTRY OF SYNTHETIC RESINS.

BY  
CARLETON ELLIS

INDUSTRIAL RESEARCH CHEMIST

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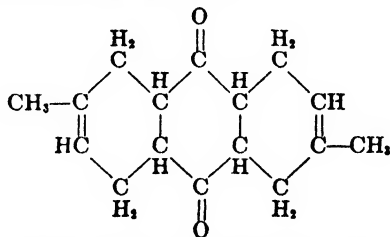
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## Chapter 40

### The Diene Synthesis

The Diels-Alder reaction has opened up a new field of synthesis of such compounds as terpenes, sesquiterpenes, camphors, alkaloids, and partially hydrogenated benzene derivatives. The direct application of this reaction to the production of resins has taken place only in certain isolated instances. Indirectly, however, the reaction has served to interpret or re-interpret mechanisms which could not otherwise be characterized and to elucidate structures, particularly as regards to whether a conjugated system does or does not exist.<sup>1</sup> The diene synthesis, as the Diels-Alder reaction is usually termed, probably is designed to play an important role in the field of synthetic resins, both in the production of special types or qualities of resins and in the study of various resinifying reactions. For this reason it has been deemed desirable to present a rather complete consideration of the chemistry involved in the formation of the products of diene synthesis (so-called adducts), a discussion of which embraces the greater part of the text of this chapter. In 1906 Albrecht<sup>2</sup> described several reactions between quinones and cyclopentadiene. He found that either one or two molecules of cyclopentadiene would combine by straight addition with benzoquinone but could not assign any satisfactory constitution to the resulting products. Somewhat later, it was noted that isoprene could likewise be condensed with benzoquinone<sup>3</sup> by heating in a sealed tube at 120-180°C. for 5 to 6 hours. The resulting product was a white crystalline substance, which added two mols of bromine and which formed a dioxime. It was suggested that the isoprene added 1,4 to the quinone and the provisional formula was assigned as



<sup>1</sup> For the use of maleic anhydride and citraconic anhydride, for example, in the purification or the isolation of new isomers and in the elucidation of the structures of ergosterol and Vitamin D, see A. Windaus, K. Dithmar, H. Murke and F. Suckfüll, *Ann.*, 1931, 485, 91; *Brit. Chem. Abs. A.*, 1931, 1051. A. Windaus, A. Lüttringhaus and M. Deppe, *Ann.*, 1931, 489, 252; *Chem. Abs.*, 1932, 26, 1016. A. Windaus and A. Lüttringhaus, *Ber.*, 1931, 64, 850; *Chem. Abs.*, 1931, 25, 4007. A. Windaus, *Proc. Roy. Soc.*, 1931, 108B, 568; *Brit. Chem. Abs. A.*, 1931, 1098. W. Stoll, *Z. physiol. Chem.*, 1901, 202, 232; *Chem. Abs.*, 1932, 26, 734. Z. Nakamiya, *Z. physiol. Chem.*, 1931, 203, 255; *Chem. Abs.*, 1932, 26, 1295.

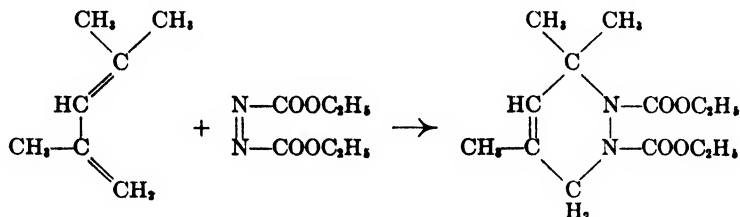
For the use of maleic anhydride to identify the diolefins in the lower fractions of vapor-phase-cracked gasoline, see S. F. Birch and W. D. Scott, *Ind. Eng. Chem.*, 1932, 24, 49. J. C. Morrell, C. G. Dryer, C. D. Lowry, Jr., and G. Egloff, *ibid.*, 1934, 26, 655; in the determination of divinyl in the presence of butylenes, see I. F. Suknevich and A. A. Chilingaryan, *J. Applied Chem. (U.S.S.R.)*, 1931, 4, 724; *Chem. Abs.*, 1932, 26, 941; and in the estimation of isoprene from rubber, see H. L. Bassett and H. G. Williams, *J.C.S.*, 1932, 3234. An apparatus for the determination of diolefin hydrocarbons in gas is described by A. A. Korotkov, *Sintet. Kauchuk*, 1933, 4, 23; *Chem. Abs.*, 1934, 28, 3028 and by H. Tropach and W. J. Mattox, *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 104.

For the characterization of the dimethylbutadienes by maleic anhydride, E. H. Farmer and F. L. Warren (*J.C.S.*, 1931, 3221) have found that the 1,3-, the 1,4- and the 2,3-dimethylbutadienes add quantitatively; the 1,3-dimethyl and the 1-methyl polymerize slightly and the 1,1-dimethyl polymerizes completely.

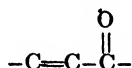
<sup>2</sup> W. Albrecht, *Ann.*, 1906, 348, 31; *J.C.S.*, 1906, 90 (1), 674.

<sup>3</sup> H. von Euler and K. O. Josephson, *Ber.*, 1920, 53, 523; *Chem. Abs.*, 1920, 14, 3342.

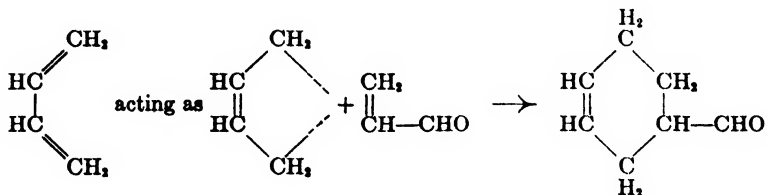
Diels, Blom and Koll<sup>4</sup> determined the structure of the reaction product of dimethylisoprene (2,4-dimethyl-1,3-pentadiene) with ethyl azocarboxylate to be diethyl 3,3,5-trimethyl- $\Delta^4$ -tetrahydro-1,2-pyridazine-1,2-dicarboxylate.



They suggested at the time that cyclopentadiene in Albrecht's reaction<sup>5</sup> reacted as a conjugated system with quinone. Later Diels and Alder<sup>6</sup> extended the scope of the reaction of the addition products of the dienes and since that time the method has been known as the "diene synthesis" or the Diels-Alder reaction.<sup>7</sup> It involves a system of conjugated double bonds reacting with the grouping



in such a manner that the conjugated double bonds are opened up at the 1,4 position and become attached to or saturate the ethylenic bond of the  $\alpha\beta$ -enal with the formation of carbon-carbon unions. The reaction of butadiene with acrolein may be represented as follows:



the final product being  $\Delta^4$ -tetrahydrobenzaldehyde.<sup>8a</sup>

This system of conjugated double bonds may be in a straight chain (butadiene, isoprene, dimethylbutadiene or myrcene), in a cyclic structure (cyclopentadiene, cyclohexadiene,  $\alpha$ -phellandrene or anthracene) or in a heterocyclic structure (furan, pyrrole). The  $\alpha\beta$ -enal grouping ( $-\text{C}=\text{C}-\overset{\text{O}}{\parallel}{\text{C}}=$ ) may be in a straight chain (acrolein, acrylic acid, crotonaldehyde) or in a ring (quinone, maleic anhydride,<sup>9</sup> itaconic anhydride or citraconic anhydride). Cyclopentadienone stands in rather an anomalous position in that it fits into both classifications. It should undergo auto-reaction; this was found to be the case in the phenyl-substituted derivative.

<sup>4</sup> O. Diels, J. H. Blom and W. Koll, *Ann.*, 1925, 443, 242; *J.C.S.*, 1925, 128 (1), 976.

<sup>5</sup> W. Albrecht, *loc. cit.*

<sup>6</sup> O. Diels and K. Alder, *Ann.*, 1928, 460, 98; *Chem. Abs.*, 1928, 22, 1144.

<sup>7</sup> For reviews on the diene synthesis, see K. Alder, "Die Methoden der Dien-synthese," Abt. I, Teil 2/11 in E. Abderhalden's "Handbuch der Biologischen Arbeitsmethoden," Urban & Schwarzenberg, Berlin and Vienna, 1933, 3079, and O. Diels, *Z. angew. Chem.*, 1929, 42, 911; *Chem. Abs.*, 1930, 24, 356. See also O. Diels and K. Alder, *U. S. P.* 1,944,731 and 1,944,732, Jan. 23, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2010, 1937, British P. 300,180, 1927; *Chem. Abs.*, 1929, 23, 3476. German P. 526,163, 1927; *Chem. Abs.*, 1931, 25, 4283.

<sup>8a</sup> Reaction of  $\alpha$ -phenylbutadiene with acrolein forms 2-phenyl- $\Delta^4$ -tetrahydrobenzaldehyde. See E. Lehmann and W. Paasche, *Ber.*, 1935, 68, 1146.

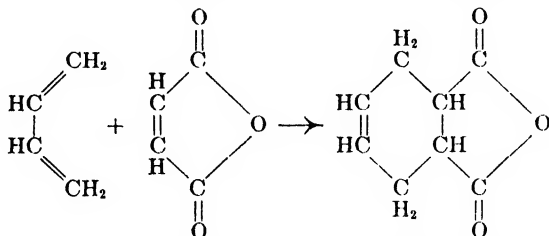
<sup>9</sup> P. Pfeiffer and T. Böttler (*Ber.*, 1918, 51, 1819; *Chem. Abs.*, 1919, 13, 1471) have discussed the quinoidal nature of maleic anhydride.

More recently, it has been shown that the acetylenic linkage will also react with the dienes. Mention has already been made of the reaction between certain azo compounds and conjugated diene hydrocarbons.

It may readily be seen that, with this form of synthesis, numerous types of compounds may be built up. The structures, which will be considered, are: first, the reaction of the dienes in a straight chain; second, the dienes in a cyclic system (both homo- and heterocyclic); and finally, the action of higher polyenes.

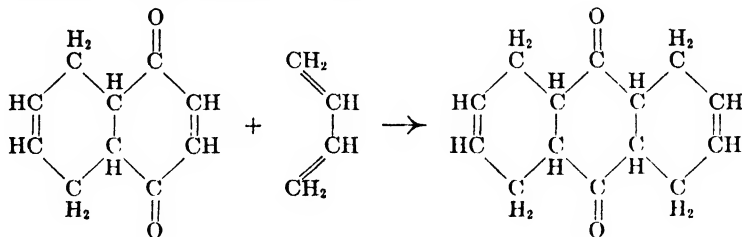
#### ACYCLIC BUTADIENOIDS

6-Methyl- $\Delta^3$ -tetrahydrobenzaldehyde\* is obtained by the action of butadiene on crotonaldehyde. By using maleic anhydride<sup>10</sup> (in place of the aldehyde) with butadiene, the cis- $\Delta^4$ -tetrahydro-o-phthalic anhydride is obtained.



Brooks and Cardarelli<sup>11</sup> prepared a light-colored resin by heating this acid (or anhydride) with glycerol.

Benzoquinone having two  $\alpha\beta$ -enal groupings may react with one or two mols of the diene to give rise to  $\Delta^{2,6}$ -tetrahydro-1,4-naphthoquinone and  $\Delta^{2,6}$ -octahydro-anthraquinone, respectively.<sup>12</sup> The tetrahydronaphthoquinone, formed from benzoquinone and butadiene, reacts with a second mol of the diene to yield the octahydroanthraquinone, as represented below:



The octahydroanthraquinones, however, are capable of isomerization when heated with acid or with alkali. When treated with alcoholates they yield hexahydroanthrahydroquinones which may be dehydrogenated to hexahydroanthraquinones.<sup>13</sup>

\* When this aldehyde (or others of like nature) is treated with acetone and sodium methoxide aldolization takes place. By dehydration, tetrahydromethyl-benzalacetone, a perfume ingredient, is obtained; see O. Diels and K. Alder, U. S. P. 1,891,043, Dec. 13, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1891. German P. 555,398, 1929; *Chem. Abs.*, 1932, 26, 3075.

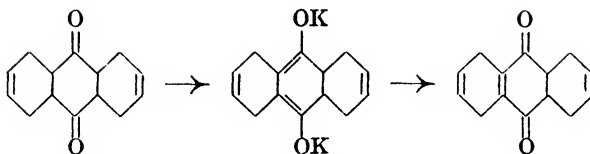
<sup>10</sup> O. Diels and K. Alder, *Ann.*, 1928, 460, 98; *Chem. Abs.*, 1928, 22, 1144.

<sup>11</sup> B. T. Brooks and E. J. Cardarelli, U. S. P. 1,860,730, May 31, 1932; *Chem. Abs.*, 1932, 26, 3945.

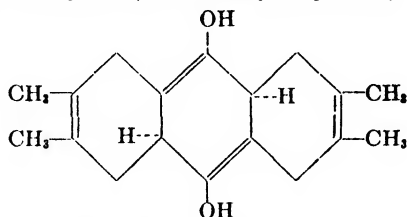
<sup>12</sup> O. Diels and K. Alder, *loc. cit.* K. Alder and G. Stein, *Ann.*, 1933, 501, 247; *Chem. Abs.*, 1933, 27, 2441. For the addition of diazomethane to quinones, see L. F. Fieser and M. A. Peters, *J.A.C.S.*, 1931, 53, 4080.

<sup>13</sup> A. Lüttringhaus, H. Neresheimer and W. Schneider, German P. 494,443, 1928, and addn. 554,878, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2757; 1933, 27, 309. French P. 36,990, 1929; 38,055, 1929; 39,333, 1930; addns. to 673,825, 1929; *Chem. Abs.*, 1931, 25, 965; 1932, 26, 604; 1932, 26, 2202; 1930, 24, 2757. British P. 320,375, 1928; 340,509, 1929; 341,553, 1929; *Chem. Abs.*, 1930, 24, 2757, 1931, 25, 4894.

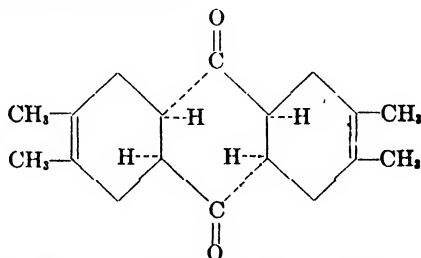




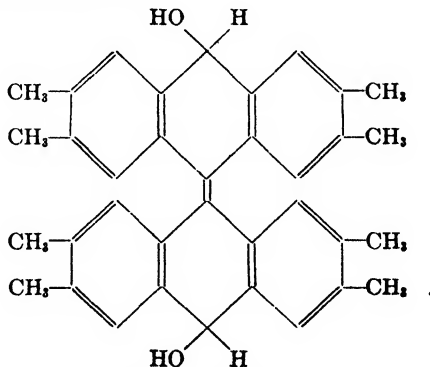
Morgan and Coulson<sup>14</sup> studied the condensation of p-benzoquinone with 2,3-dimethylbutadiene-1,4. Their product, 2,3,6,7-tetramethyl- $\Delta^{2,6}$ -octahydroanthraquinone, isomerizes when treated with acid or alkali or when recrystallized from a high-boiling solvent. Since it could not be acetylated, it was not regarded as 2,3,6,7-tetramethyl- $\Delta^{2,6}$ -hexahydro-9,10-anthrahydroquinone,



but rather as the isomeric derivative:



By passing oxygen through an alcoholic solution of this compound, 2,3,6,7-tetramethyl anthraquinone is formed which on reduction passes into 2,3,6,7-tetramethyl anthrone; the indications are, however, that this loses water to yield 2,3,6,7,2',3',6',7'-octamethyl-10,10'-dihydro-dianthrol,

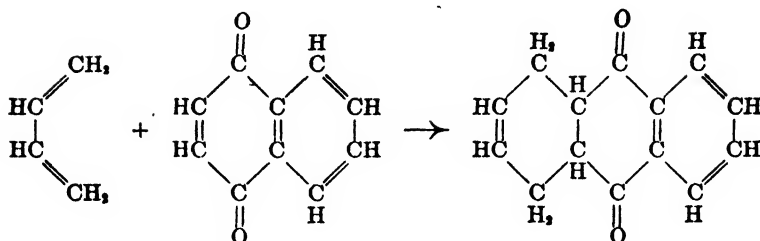


1,3-Butadienes also react with  $\alpha$ -naphthoquinones<sup>15</sup> or with the halogenated derivatives<sup>16</sup> (2-chloro- and 2,3-dichloro-1,4-naphthoquinones) to form tetrahydronaphthoquinones (or derivatives).

<sup>14</sup> G. T. Morgan and E. A. Coulson, *J.C.S.*, 1931, 2323.

<sup>15</sup> O. Diels and K. Alder, *Ann.*, 1928, 450, 110; *Chem. Abs.*, 1928, 22, 1144. *Ber.*, 1929, 62, 2365.

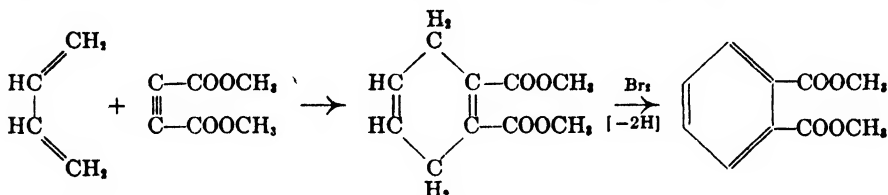
<sup>16</sup> French P. 37,684, 1929, addn. to 673,825, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4559.



Isomerization can take place as in the case of the octahydroanthraquinones, or for the corresponding halogenated compounds, by an intermolecular elimination of halogen acid. If an oxidizing agent (nitrobenzene) is used initially in the reaction of butadiene with naphthoquinone, anthraquinone itself is obtained.<sup>17</sup>

Tetrahydroquinazarine (1,4-dihydroxy- $\Delta^4$ -tetrahydroanthraquinone) is formed from butadiene and naphthazarin (5,8-dihydroxy-1,4-naphthoquinone).<sup>18</sup>

Butadiene combines with methyl acetylenedicarboxylate in the manner of a 1,4 addition to yield a derivative which on dehydrogenation passes over into



phthalic ester.<sup>19</sup> It is of interest to note that triphenylmethyl combines both with isoprene and with dimethylbutadiene, with the addition taking place 1,4.<sup>20</sup>

The butadiene acids (sorbic<sup>21</sup> and muconic) yield, with maleic anhydride carboxylate, tetrahydrophthalic anhydrides.<sup>22</sup>

### CYCLIC BUTADIENOIDS

Cyclopentadiene and acrolein form 2,5-endomethylene- $\Delta^3$ -tetrahydrobenzaldehyde which on reduction passes into 2,5-endomethylene-hexahydrobenzaldehyde,<sup>23</sup> the semicarbazone of which on treatment with sodium acetate and acetic anhydride yields enol-norcamphenilanaldehyde acetate; this on ozonolysis and hydrolysis decomposes into norcamphor.<sup>24</sup>

<sup>17</sup> G. Kränzlein, H. Dieterle and H. Vollmann, German P. 544,522, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3522.

<sup>18</sup> O. Diels and K. Alder, German P. 544,523, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3523. For other quinazarins, see G. Kränzlein, H. Dieterle and H. Vollmann, German P. 544,522, 1929. H. Dieterle, A. Salomon and E. Nossek, *Ber.*, 1931, 64, 2090. For the colored compounds which are obtained by the condensation of methylenanthrone with quinones and with compounds containing the ethylene or the enol ( $-\text{CH}=\text{C}(\text{OH})-$ ) grouping, activated by an adjacent carbonyl, see British P. 405,949 and 405,967, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1934, 355. German P. 591,496 and addn., 597,525, 1934; *Chem. Abs.*, 1934, 28, 2366, 5082.

<sup>19</sup> O. Diels, K. Alder and H. Nienberg, *Ann.*, 1931, 490, 236; *Brit. Chem. Abs. A*, 1932, 55.

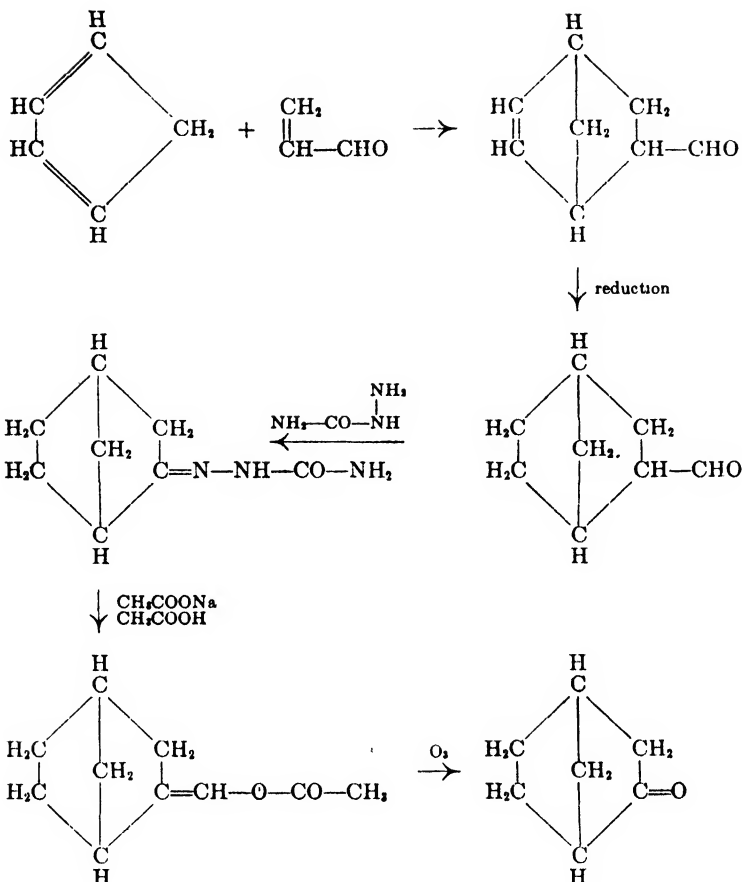
<sup>20</sup> J. B. Conant and H. W. Scherp, *J.A.C.S.*, 1931, 53, 1941.

<sup>21</sup> For the decarboxylation of sorbic acid with barium hydroxide, see R. Kuhn and A. Deutsch, *Ber.*, 1932, 65, 43; *Chem. Abs.*, 1932, 26, 2174. Under the treatment, sorbic acid yields o-propyltoluene. Decarboxylation of vinylacrylic acid ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{COOH}$ ) gives in part ethylbenzene, while dinnamylacrylic acid gives  $\beta$ -phenyl- $\alpha$ -o-diphenylethane. An unsaturated aliphatic carboxylic acid containing a double bond in the  $\alpha$ -position (crotonic or sorbic acid), when incorporated into paints along with drying oil, diluent, drier and pigment produces a paint of improved flow. See H. Bernard, U. S. P. 1,533,274, Nov. 24, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 807.

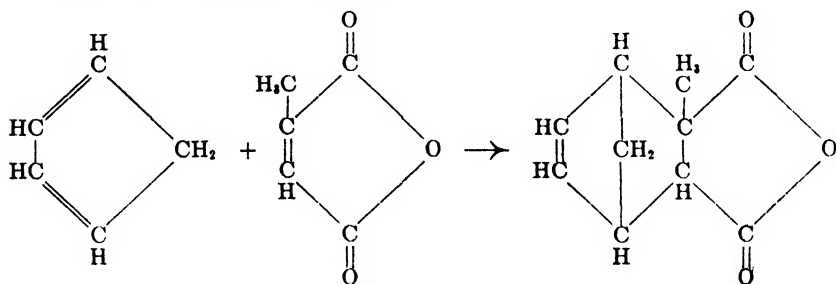
<sup>22</sup> E. H. Farmer and F. L. Warren, *J.C.S.*, 1929, 897.

<sup>23</sup> O. Diels and K. Alder, *Ann.*, 1928, 460, 98; *Chem. Abs.*, 1928, 22, 1144.

<sup>24</sup> O. Diels, K. Alder, W. Lübbert, E. Naujok, F. Querberis, K. Röhl and H. Segeberg, *Ann.*, 1929, 470, 62; *Chem. Abs.*, 1929, 23, 3692.

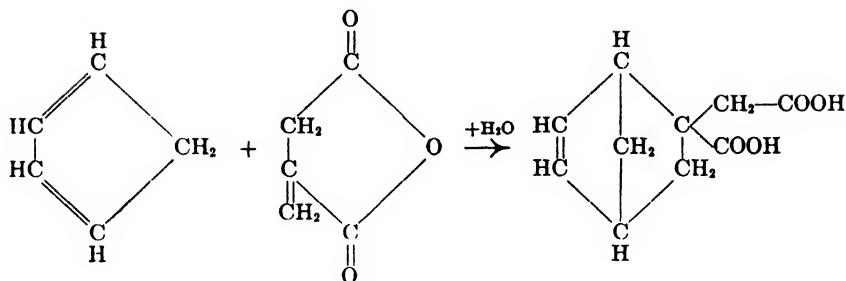


Cyclopentadiene reacts vigorously and quantitatively with maleic anhydride. The compound formed under these conditions is also a bridged anhydrocyclohexene, 3,6-endomethylene- $\Delta^4$ -tetrahydrophthalic anhydride.<sup>28</sup> Citraconic anhydride yields the corresponding 1-methyl derivative

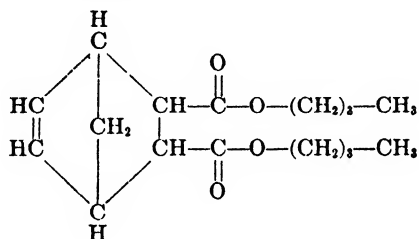


while itaconic anhydride yields a 2,5-endomethylene- $\Delta^2$ -cyclohexenylidene succinic acid,

<sup>28</sup> For the resinification of this derivative on treatment with permanganate, see E. H. Farmer and F. L. Warren, *J.C.S.*, 1929, 907.

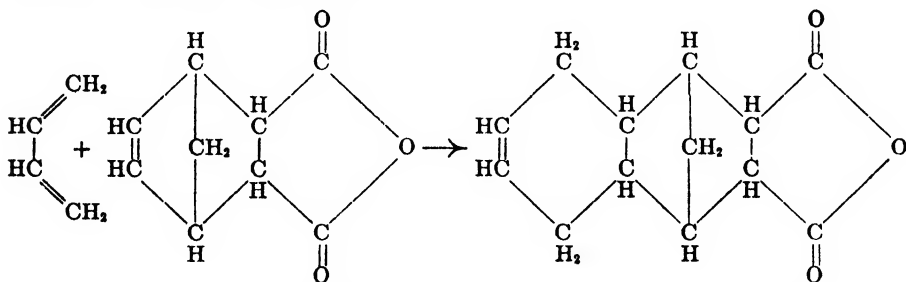


Crude benzol contains among other substances cyclopentadiene. By treating benzol with maleic anhydride, the dienes are removed and the dibasic acid anhydride formed has been suggested as a base for resins.<sup>26</sup> The dibutyl ester of 3,6-endomethylene- $\Delta^4$ -phthalic anhydride



has been recommended as a plasticizer in nitrocellulose lacquers.<sup>27</sup>

Alder and Stein<sup>28</sup> have shown that the adduct of maleic anhydride and cyclopentadiene will further react with butadiene with the production of a bridged octahydronaphthalene derivative,



1,4-endomethylene- $\Delta^6$ -octahydro-2,3-naphthalene-2,3-dicarboxylic anhydride.

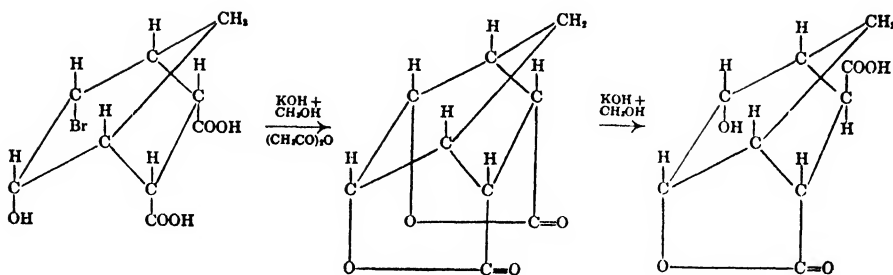
The substituted derivative of endomethylene hydrophthalic acid or 4-bromo-5-hydroxy-cis-3,6-endomethylenehexahydrophthalic acid is converted by means of 25 per cent alcoholic potassium hydroxide, followed by acetic anhydride, into the dilactone of 4,5-dihydroxy-cis-3,6-endomethylenehexahydrophthalic acid. This compound can be distilled unchanged and is not affected by hot concentrated nitric acid. Rearrangement occurs, however, with alcoholic potash into the trans-lactonic acid.<sup>29</sup>

<sup>26</sup> British P. 352,164, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3261.

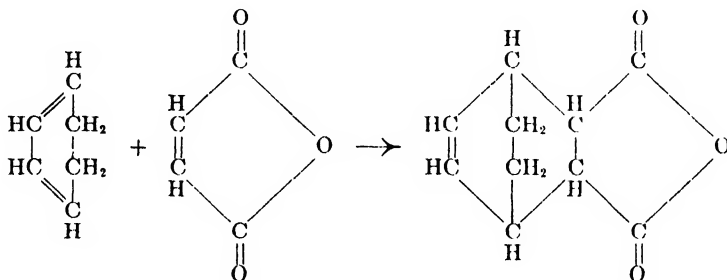
<sup>27</sup> O. Jordan and H. Krsikalla, German P. 543,823, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3377.

<sup>28</sup> K. Alder, G. Stein, J. Reese and W. Grassman, *Ann.*, 1932, 496, 204; *Brit. Chem. Abs. A*, 1932, 938.

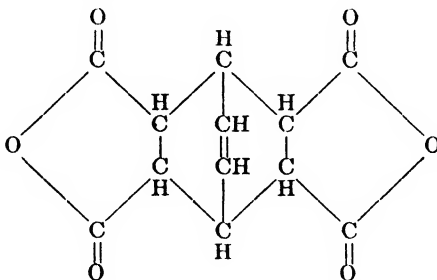
<sup>29</sup> K. Alder and G. Stein with F. von Buddenbrock, W. Eckardt, W. Frerks and S. Schneider, *Ann.*, 1934, 514, 1; *Brit. Chem. Abs. A*, 1935, 211.



By condensing maleic anhydride with cyclohexadiene (1,2-dihydrobenzene), a compound, 3,6-endo-ethylene- $\Delta^4$ -phthalic anhydride, is obtained whose bridge consists of two members.



An unsaturated bridge may also be formed by the condensation of cis-cyclohexadiene- $\Delta^{3,6}$ -1,2-dicarboxylic anhydride with maleic anhydride to 3,6-endodimethinehexahydro-tetracarboxylic anhydride.



Moreover, two mols of cyclopentadiene react with one mol of benzoquinone<sup>30</sup> to yield a compound which possesses two bridges, 1,4,5,8-di-endomethylene- $\Delta^{3,6}$ -octahydroanthraquinone.<sup>31</sup> Similarly with cyclohexadiene the di-endoethylene compound is obtained.<sup>32</sup>

Both cyclopentadiene and cyclohexadiene react with methyl acetylenedicarboxylic ester. The former yields dimethyl-3,6-endomethylene-3,6-dihydrophthalate; the latter forms a similar endoethylene compound.<sup>33</sup> On reduction the double bond

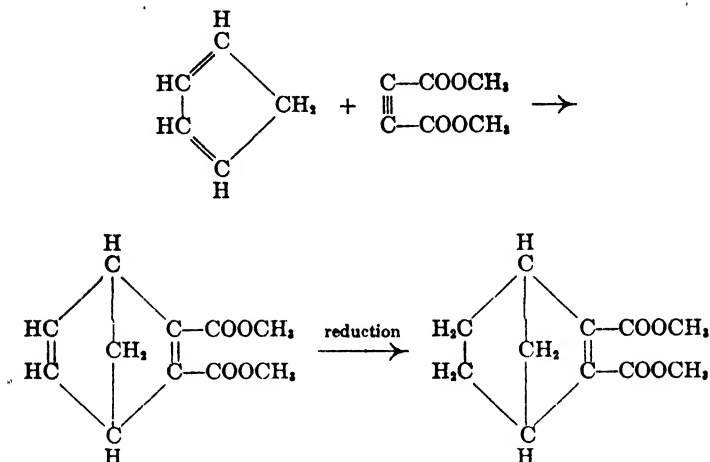
<sup>30</sup> A. Wassermann (*Ber.*, 1933, 66, 1392; *Chem. Abs.*, 1934, 28, 25) has measured the velocity of the reaction of quinone with cyclopentadiene to form monocyclopentadienequinone. The velocity is followed by color change inasmuch as the quinone is more highly colored than the final product. The reaction is found to be bimolecular in *n*-hexane, in carbon tetrachloride, in benzene, in ethanol and in acetic acid.

<sup>31</sup> Cf. W. Albrecht, *loc. cit.*

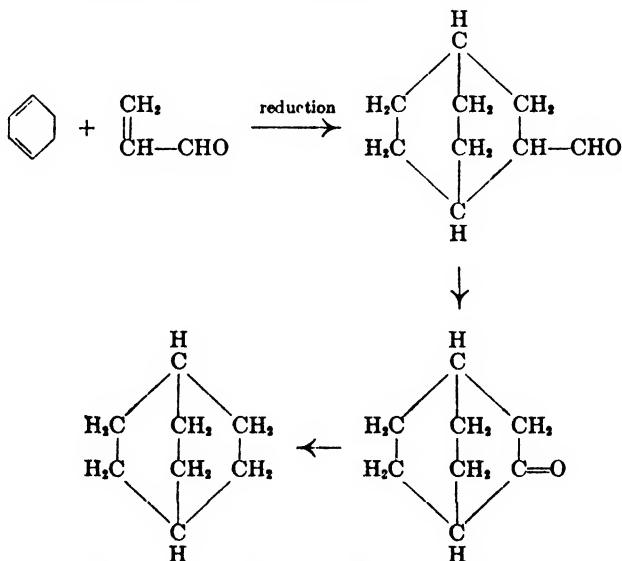
<sup>32</sup> O. Diels and K. Alder, *Ann.*, 1928, 460, 98; *Chem. Abs.*, 1928, 22, 1144.

<sup>33</sup> O. Diels, K. Alder and H. Nienberg, *Ann.*, 1931, 490, 236; *Chem. Abs.*, 1933, 26, 436.

between the ester groups is unaffected whereas the other bond is reduced. The reaction may be expressed



Cyclohexadiene combines with acraldehyde at 100°C. to yield 2,5-endoethylene- $\Delta^2$ -tetrahydrobenzaldehyde, the semicarbazone of which is reduced to the semicarbazone of 2,5-endoethylene-hexahydrobenzaldehyde. Subsequent treatment with acetic anhydride and sodium acetate and fission with ozone of the resulting enol-acetate yields 2,5-endoethylene-cyclohexanone.<sup>44</sup> Reduction of the 2,5-endoethylene-cyclohexanone by the Wolff-Kishner method, that is, using sodium and alcohol in the presence of semicarbazone, results in the preparation of 2,2,2-dicyclo-octane.<sup>45</sup>

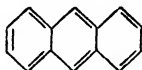


Anthracene possesses diene properties to such an extent that it will react with

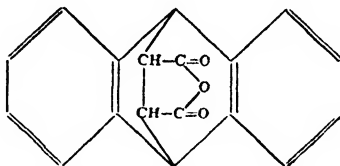
<sup>44</sup> O. Diels, K. Alder, E. Petersen and F. Querberitz, *Ann.*, 1930, 478, 137.

<sup>45</sup> K. Alder, G. Stein, F. von Buddenbrock, W. Freerks and S. Schneider, *Ann.*, 1934, 514, 1; *Brit. Chem. Abs. A*, 1935, 211. For the preparation of 1,2,2-dicycloheptane, see G. Komppa and S. Beckmann, *Ann.*, 1934, 512, 172; *Brit. Chem. Abs. A*, 1934, 1103.

$\alpha\beta$ -enal structures and with acetylenedicarboxylic acid to yield endo compounds.<sup>80</sup> Diels and Alder<sup>81</sup> represent anthracene as a system of conjugated double bonds

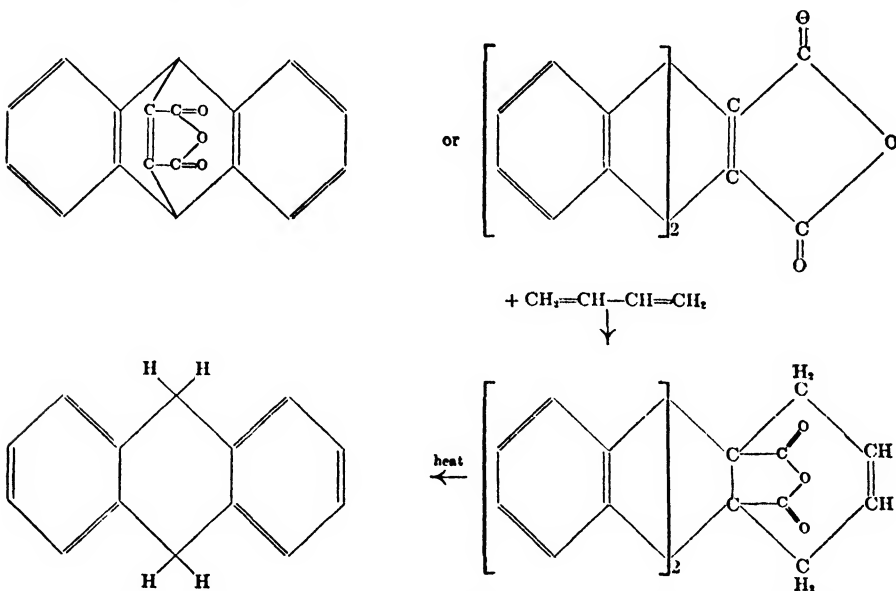


and the addition with maleic anhydride affords 9,10-endoanthracene- $\alpha,\beta$ -succinic anhydride,



which on oxidation reverts to anthraquinone.

Anthracene-acetylenedicarboxylic anhydride, similarly prepared, contains an unsaturated bridge and can further react with butadiene, 1,1,3-trimethylbutadiene and cyclopentadiene to yield complex adducts. With butadiene, the reaction may be written as follows:



Decomposition of the adduct by heat results in the formation of dihydroanthracene and phthalic anhydride. Heating the anthracene-acetylenedicarboxylic acid in nitrobenzene or phenol gives rise to carbon monoxide, carbon dioxide and a com-

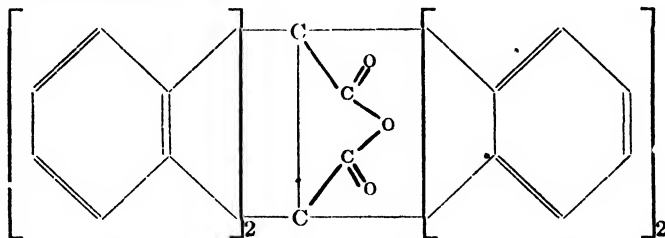
<sup>80</sup> Other hydrocarbons (toluene, ethylbenzene, isopropylbenzene, tetrahydronaphthalene, diethylbenzene and 3-methylnaphthalene) react with maleic anhydride although not through a diene reaction. The reaction occurs at about 300° under pressure. Toluene and maleic anhydride yield benzyl succinic acid; ethylbenzene and maleic anhydride give rise to a product which reverts to  $\gamma$ -methyl- $\gamma$ -phenylpyrotartaric acid,



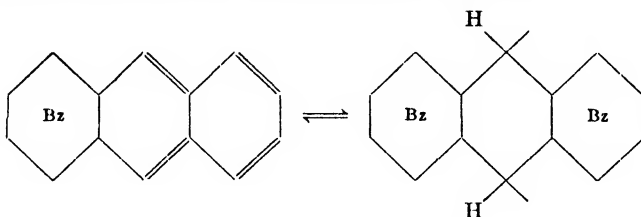
See J. Binapff, German P. 607,880, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1334

<sup>81</sup> O. Deils, K. Alder and S. Beckman, *Ann.*, 1931, 485, 191; *Chem. Abs.*, 1931, 25, 3046. See G. Kalischer and H. Scheyer, German P. 539,532, 1927, addn. to 499,590, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2301.

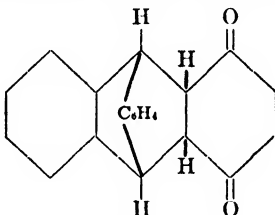
pound (m.p. 360°C.) which is stable toward potassium hydroxide, concentrated nitric acid, acetic anhydride, aniline and quinoline. This compound appears to be one in which the maleic anhydride residue is sandwiched between two anthracene molecules at the 9,10 position.<sup>39</sup>



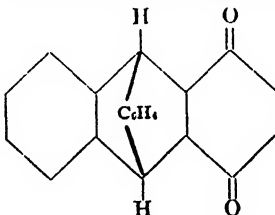
Clar<sup>39</sup> feels that the above constitution of anthracene (p. 839) is inadequate and prefers to express the structure by the equilibrium formulas:



He comes to this conclusion partly from the observation that 9,10-endoanthracene- $\alpha\beta$ -succinic anhydride dissociates into maleic anhydride and anthracene at 250-270°C. and partly from the reaction of anthracene with p-benzoquinone in boiling xylene. In the latter instance p-benzoquinone-anthracene is formed



oxidation of which yields endo-9,10-o-phenylene-9,10-dihydro-1,4-anthraquinone



Anthracene also condenses with acrylic acid or with  $\alpha$ - or with  $\beta$ -dichloropropionic acid.<sup>40</sup>

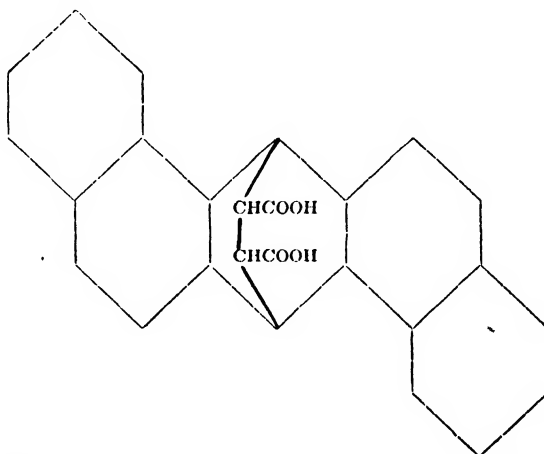
<sup>39</sup> O. Diels and W. Friedrichsen, *Ann.*, 1934, 513, 145; *Brit. Chem. Abs. A*, 1934, 1351.

<sup>39</sup> E. Clar, *Ber.*, 1931, 64, 1676, 2193; *Brit. Chem. Abs. A*, 1931, 1044, 1292. For Diels and Alder's reply see *Ber.*, 1931, 64, 2116; *Brit. Chem. Abs. A*, 1931, 1282.

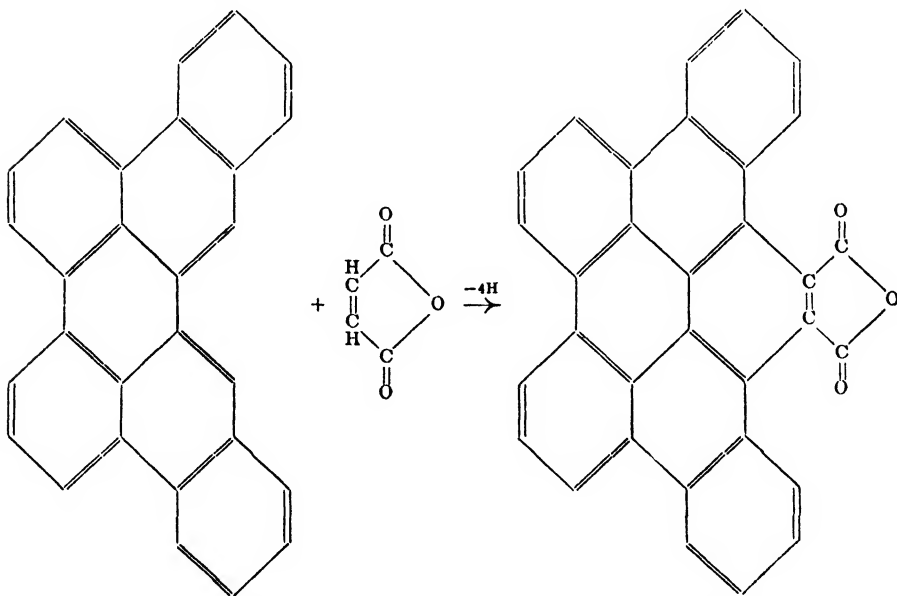
<sup>40</sup> G. Kalischer and H. Scheyer, U. S. P. 1,836,123, Dec. 15, 1931, to Winthrop Chemical Co.; *Chem. Abs.*, 1932, 26, 1130.



1,2,5,6-Dibenzanthracene reacts with maleic anhydride but the action is much more sluggish. On hydrolysis, 1,2,5,6-dibenzanthracene-9,10-endo- $\alpha\beta$ -succinic acid is obtained.<sup>41</sup>



In boiling xylene, perylene appears to form an addition compound with maleic anhydride, on cooling, however, the hydrocarbon separates unchanged. 2,3-10,11-Dibenzoperylene reacts in the following manner with maleic anhydride in boiling nitrobenzene:

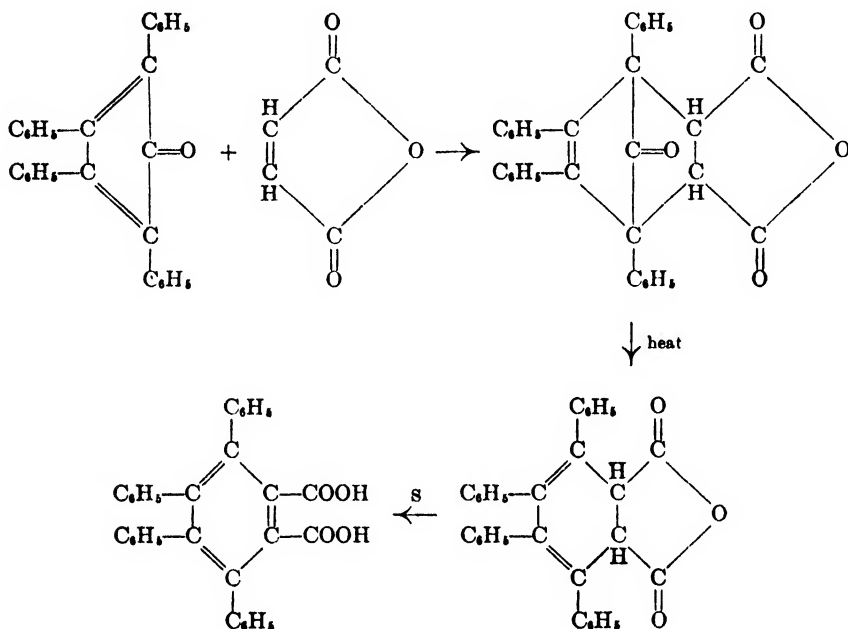


Under similar conditions, neither phenanthrene nor benzanthrone react with maleic anhydride.<sup>42</sup> In the above reaction between dibenzoperylene and maleic anhydride, nitrobenzene acts as a mild oxidizing agent.

<sup>41</sup> J. W. Cook, *J.C.S.*, 1931, 3373.

<sup>42</sup> E. Clar (in part with W. Hempel), *Ber.*, 1932, 65, 846; *Brit. Chem. Abs. A*, 1932, 731.

Tetraphenylcyclopentadienone has been used with maleic acid to build highly arylated systems. 3,6-Endocarbonyl-3,4,5,6-tetraphenyl- $\Delta^4$ -dihydrophthalic acid anhydride is obtained, which on decarboxylation yields 1,2,3,4-tetraphenyl benzene.<sup>48</sup> The derivative formed by the action of maleic anhydride on tetraphenylcyclopentadienone namely, 3,6-endocarbonyl-3,4,5,6-tetraphenyl-1,2-dihydrophthalic anhydride loses carbon monoxide on heating to yield 3,4,5,6-tetraphenyl-1,2-dihydrophthalic anhydride which may be dehydrogenated by sulphur.<sup>48</sup>



Depending on the temperature at which the addition of maleic anhydride takes place, different compounds are formed. In boiling benzene, tetraphenylcyclopentadienone and maleic anhydride yield the endo derivative; in chlorobenzene, the hydrated phthalic acid is obtained; whereas in nitrobenzene, tetraphenylphthalic anhydride results. The accumulation of phenyl groups hinders the reactivity of tetraphenylphthalic anhydride; it does not dissolve in aqueous ammonium hydroxide and is not esterified with ethanol. When esters are prepared, that is, by the action of tetraphenylcyclopentadienone on the dialkyl ester of acetylene dicarboxylic acid, the esters can not be hydrolyzed.<sup>48</sup>

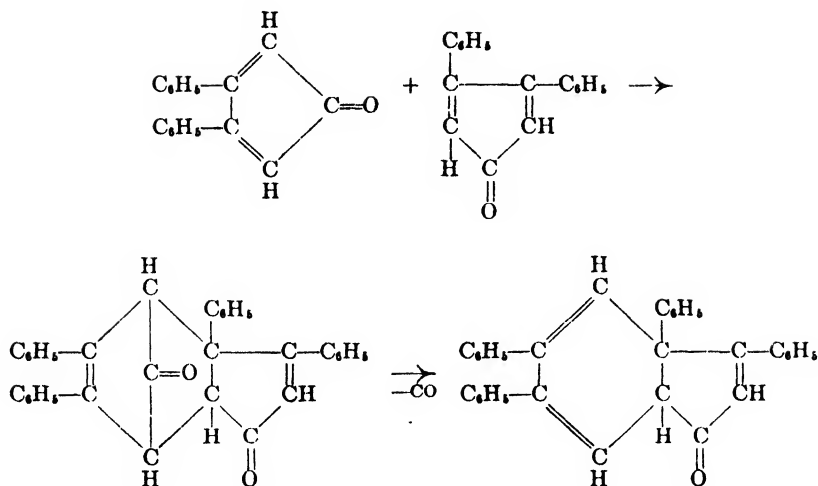
Two mols of 3,4-diphenylcyclopentadienone undergo auto-reaction, yielding a diketone; the latter is also formed by dehydration of anhydroacetonebenzil (4-hydroxy-3,4-diphenyl- $\Delta^2$ -cyclopentenone).<sup>48</sup> The diketone splits out carbon monoxide when heated, forming a ketone as shown in the equation on page 843. Further heating results in rearrangement to 2,3,5,6-tetraphenylhydrindone.

<sup>48</sup> W. Diltthey, W. Schommer and O. Trötschel, *Ber.*, 1933, 66, 1637.

<sup>48</sup> C. F. H. Allen and L. J. Sheps, *Can. J. Research*, 1934, 11, 171; *Chem. Abs.*, 1935, 29, 142.

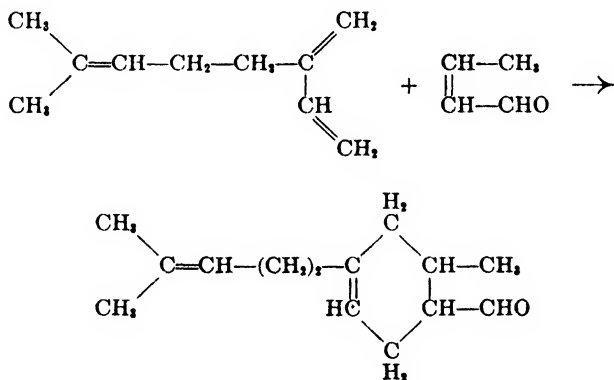
<sup>48</sup> W. Diltthey, I. Thewalt and O. Trötschel, *Ber.*, 1934, 67, 1959; *Chem. Abs.*, 1935, 29, 1799.

<sup>48</sup> C. F. H. Allen and E. W. Spanagel, *Can. J. Research*, 1933, 8, 414; *Brit. Chem. Abs. A*, 1933, 823. See F. R. Japp and C. I. Burton, *J.C.S.*, 1887, 51, 426.



## TERPENOIDS

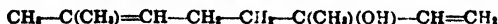
Myrcene, 6-methyl-2-vinyl-1,5-heptadiene, an acyclic terpene, possesses a conjugate linkage and will react with either crotonic aldehyde or with maleic anhydride. With the aldehyde, myrcene yields a partially hydrogenated benzaldehyde,



6-methyl-3-isohexenyl- $\Delta^4$ -tetrahydrobenzaldehyde. With maleic anhydride, 4-isohexenyl-cis- $\Delta^4$ -tetrahydrophthalic anhydride can be synthesized.<sup>47</sup>

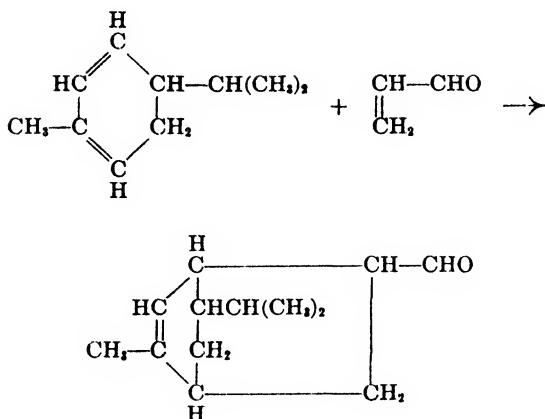
A cyclic terpenoid under the same conditions gives rise to a branched bridge. For example, with  $\alpha$ -phellandrene and acrolein, 2,5-endo-isoamylene-1,2,5,6-tetrahydro-1-benzaldehyde is obtained.<sup>48</sup>

<sup>47</sup> The melting point of the corresponding acid is 122-3°C. B. A. Arbusov and U. S. Abramov (*Ber.*, 1934, 67, 1942; *Chem. Abs.*, 1935, 29, 1384) dehydrated linalool,



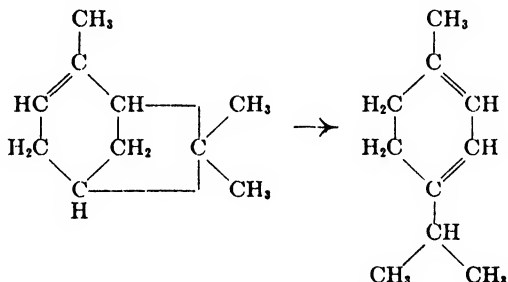
and condensed the dehydrated product (which should be myrcene) with maleic anhydride and obtained the acid which melted much lower (111-113.5°C.). Attempts to isomerise the acid with hydrogen bromide into dimethyloctahydronaphthalene-6,7-dicarboxylic acid were unsuccessful; an uncrystallizable oil resulted.

<sup>48</sup> O. Diels, K. Alder, W. Lübbert, E. Naujoks, F. Querberits, K. Röhl and H. Segeberg, *Ann.*, 1929, 470, 62; *Chem. Abs.*, 1929, 23, 3692. B. A. Arbusov (*Ber.*, 1934, 67, 563; *Chem. Abs.*, 1934, 28, 4402) isomerised  $\alpha$ -pinene to an aliphatic terpene by passing the vapors of the pinene over reduced copper or



The reaction product of  $\alpha$ -terpinene and maleic anhydride has found use in the production of safety glass,<sup>49</sup> whereas the resin obtained by heating  $\alpha$ -terpinene, maleic anhydride and abietic acid at 125-250°C. has been suggested for varnishes.<sup>50</sup>

$\alpha$ -Terpinene may be derived from pinene, dipentene,  $\alpha$ -terpineol and terpenehydrate by means of sulphuric acid. By gradually treating 2 liters of pinene with 70 cc. of sulphuric acid, rearrangement takes place. Neutralization with alkali together with steam distillation and fractionation yields  $\alpha$ -terpinene.



When 480 parts of  $\alpha$ -terpinene are heated with 294 parts of maleic anhydride at 150-200°C. for 5 hours and the reaction mixture is subjected to vacuum évaporation, a soft amorphous solid is obtained.<sup>51</sup> Esterification of 1 mol of the resulting terpinene-maleic anhydride with 4 mols of butyl alcohol at 117°C. for 4 hours yields the monobutyl terpinene-maleate. If sulphuric acid is added, dibutyl terpinene-maleate results. Esterification with glycol yields a pale yellow, resinous solid soluble in acetone, toluene and butyl acetate whereas esterification with glycerol gives rise to a hard and brittle resin.<sup>52</sup> Terpinene-maleic anhydride can

through tubes filled with fragments of Suprax glass at 340°. A synthesis was undertaken to prove the structure of the isomeric derivative to be alloöcimene (*ibid.*, 569). Meanwhile F. G. Fischer and K. Löwenberg (*Ber.*, 1933, 66, 669; *Chem. Abs.*, 1933, 27, 3446) had synthesized alloöcimene from 2-methyl-2,4-heptadien-6-one and  $\alpha$ -bromoethyl propionate by means of the Reformatsky reaction and definitely deduced that alloöcimene was 2,6-dimethyl-2,4,6-octatriene [(CH<sub>3</sub>)<sub>2</sub>C=CH-CH=CH-C(CH<sub>3</sub>)<sub>2</sub>=CH-CH<sub>3</sub>]. B. A. Arbuzov (*Ber.*, 1934, 67, 1946; *Chem. Abs.*, 1935, 29, 1407) then determined that the maleic anhydride addition compound of alloöcimene was identical with the maleic anhydride addition product of isomerized  $\alpha$ -pinene.

<sup>49</sup> G. H. Peters, U. S. P. 1,832,298, Oct. 11, 1932, to Hercules Powder Co.; *Chem. Abs.*, 1933, 27, 824.

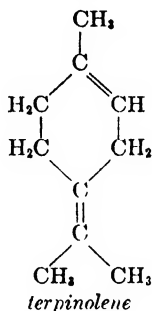
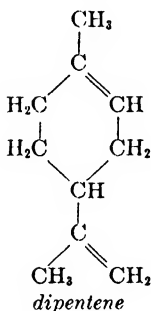
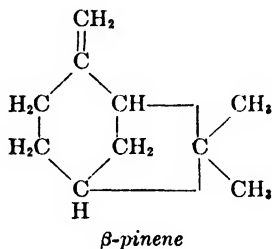
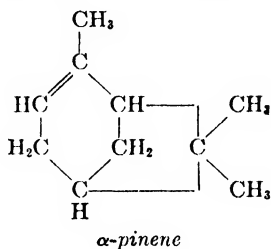
<sup>50</sup> E. G. Peterson, U. S. P. 1,978,598, Oct. 30, 1934, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 254.

<sup>51</sup> E. G. Peterson and E. R. Littmann, U. S. P. 1,993,025, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2623.

<sup>52</sup> E. R. Littmann, U. S. P. 1,993,026, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2623. For further discussion of this type of resin see Chapters 41-49.

be reacted with glycerol in the presence of rosin or with linseed or tung oil acids.<sup>53</sup> The terpene-maleate may be formed by heating at 200°C. 165 parts of abietic acid, 98 parts of maleic anhydride and 85 parts of  $\alpha$ -terpinene. The derivative so prepared may be further esterified with methanol in the presence of sulphuric acid,<sup>54</sup> or with glycerol in the presence of stearic acid.<sup>55</sup>

Terpenes containing no conjugated double bonds react with maleic anhydride or with fumaric acid which rearranges into maleic anhydride when heated. The terpenes which will undergo this reaction include  $\alpha$ -pinene,  $\beta$ -pinene, dipentene (and its isomers d- and l-limonene) and terpinolene.



When 400 parts of  $\alpha$ -pinene and 100 parts of maleic anhydride are heated in an autoclave at 170-175°C. under 5-10 pounds pressure for 3 hours, a soft yellow-colored acidic resin is obtained<sup>56</sup> which may be esterified with glycerol monomethyl ether,<sup>57</sup> glycerol, polyglycerol or glycol.<sup>58</sup> Pinene-maleic anhydride on saponification does not yield an alcohol, indicating that a carbon-carbon union has been formed. p-Toluenesulphonic acid assists the union of maleic anhydride and pinene<sup>59</sup> but at the same time causes rearrangement of the terpene.<sup>60</sup> By heating 100 parts of  $\alpha$ -pinene, 165 parts of abietic acid and 98 parts of maleic anhydride, a resin is formed having an acid number of 250, the acidity of which may be reduced by esterification with glycerol.<sup>61</sup>

<sup>53</sup> E. G. Peterson, U. S. P. 1,993,027 and 1,993,028, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2623.

<sup>54</sup> E. G. Peterson, U. S. P. 1,993,029, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2623.

<sup>55</sup> E. G. Peterson, U. S. P. 1,993,030, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2623.

<sup>56</sup> E. G. Peterson, U. S. P. 1,993,031, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2623.

<sup>57</sup> E. G. Peterson, U. S. P. 1,993,032, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2624.

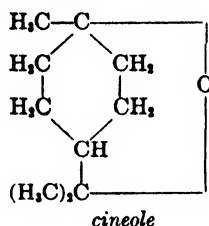
<sup>58</sup> E. G. Peterson, U. S. P. 1,993,033, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2624.

<sup>59</sup> I. W. Humphrey, U. S. P. 1,993,034, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2624.

<sup>60</sup> E. R. Littmann, U. S. P. 1,993,035, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2627.

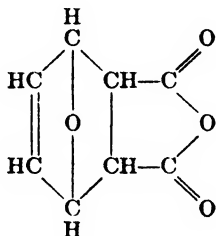
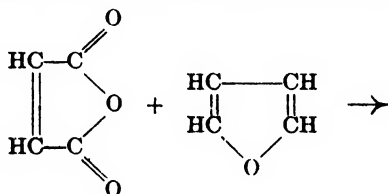
<sup>61</sup> I. W. Humphrey, U. S. P. 1,993,036, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2624.

Cineole also reacts with maleic anhydride in the presence of xylene and zinc chloride at 140°C. Purification through steam distillation and heating to 100-150° yields a light-colored, waxy solid.<sup>42</sup>

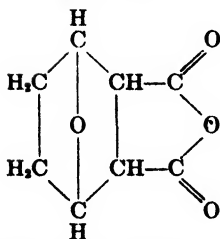


### HETEROCYCLIC OXYGEN COMPOUNDS

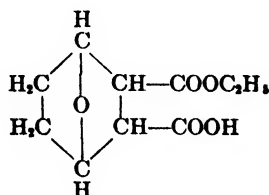
Furan will react with maleic acid in water solution<sup>43</sup> or with maleic anhydride in ether.<sup>44</sup> In the latter case there is obtained 3,6-endoxo- $\Delta^4$ -tetrahydrophthalic anhydride which on reduction with palladium in alcoholic solution gives rise to ethyl hydrogen 3,6-endoxo-hexahydrophthalate, whereas alkaline reduction affords



alkaline  
reduction ↙



↘ Pd  
reduction



3,6-endoxo-hexahydrophthalic anhydride or norcantharidin.<sup>45</sup> Moreover, the un-

<sup>42</sup> E. R. Littmann, U. S. Patent 1,993,037, Mar. 5, 1935, to Hercules Powder Co.; *Chem. Abs.*, 1935, 29, 2627.

<sup>43</sup> O. Diels, K. Alder, K. Nienburg and O. Schmalbeck, *Ann.*, 1931, 490, 243; *Brit. Chem. Abs. A.*, 1931, 1436.

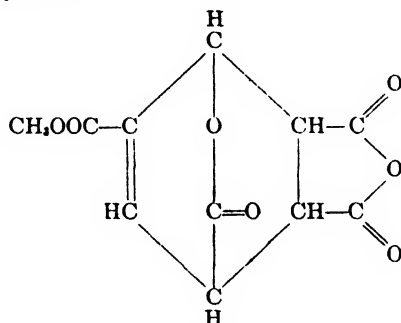
<sup>44</sup> O. Diels and K. Alder, *Ber.*, 1929, 62, 554; *Brit. Chem. Abs. A.*, 1929, 570.

<sup>45</sup> See, e.g., F. v. Bruchhausen and H. W. Versch, *Arch. Pharm.*, 1929, 266, 297; *Chem. Abs.*, 1929, 23, 1647.

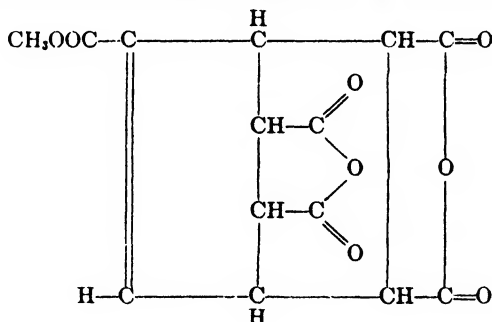
saturated phthalic anhydride derivatives react with phenyl azide<sup>66</sup> to produce triazole derivatives which find use as intermediates for drugs.

With 2,5-dimethylfuran, 3,6-endo-3,6-dimethyl- $\Delta^4$ -tetrahydrophthalic anhydride is formed.<sup>67</sup> Rinkes<sup>68</sup> prepared 3-methylfuran and this likewise reacted with maleic anhydride to give 3,6-endo-4-methyl- $\Delta^4$ -tetrahydrophthalic anhydride. 2-Methylfuran yielded 3,6-endo-3-methyl- $\Delta^4$ -tetrahydrophthalic anhydride.

In boiling toluene, methyl coumalate also forms an adduct with maleic anhydride, giving a 30 per cent yield of 3,6-endo-carboxy-4-methyl-carboxylate- $\Delta^4$ -tetrahydrophthalic anhydride.



In boiling xylene, however, a 30 per cent yield of 3,6-endo-succinic-anhydride-4-methyl-carboxylate- $\Delta^4$ -tetrahydrophthalic anhydride is obtained.<sup>69</sup>



#### HETEROCYCLIC NITROGEN COMPOUNDS

Although pyrrole is a diene system, it behaves differently with maleic anhydride than its oxygen analogue, furan. Diels and Alder<sup>70</sup> found that maleic anhydride and pyrrole react at room temperature to give only a small quantity of pyrrole-dipropionic acid; dilevulic acid (4,7-decandion-1,10-dioic acid), however, could be isolated in quantity. The mechanism of the reaction was studied with 2-methylpyrrole which yields 2-methylpyrrole-5-succinic acid. This acid readily loses carbon dioxide to form 2-methylpyrrole-5-propionic acid.

<sup>66</sup> K. Alder and G. Stein, German P. 557,238, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1003. K. Alder, G. Stein and W. Friedrichsen (*Ann.*, 1933, 501, 1; *Chem. Abs.*, 1933, 27, 2139) discuss in some detail the conditions necessary for the addition of phenyl azide to an unsaturated system.

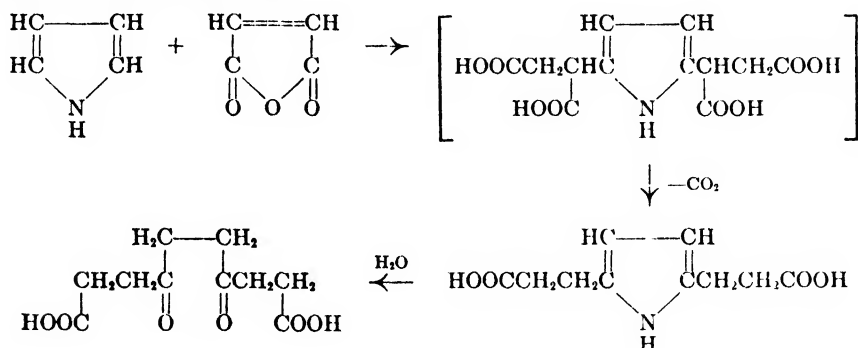
<sup>67</sup> O. Diels and K. Alder, *Ber.*, 1929, 62, 554; *Brit. Chem. Abs. A.*, 1929, 570.

<sup>68</sup> J. Rinkes, *Rec. trav. chim.*, 1931, 50, 1127; *Chem. Abs.*, 1932, 26, 1279. For another synthesis of 3-methylfuran, see T. Reichstein and H. Zschokke, *Helv. Chim. Acta*, 1931, 14, 1270; *Brit. Chem. Abs. A.*, 1932, 166.

<sup>69</sup> O. Diels, K. Alder and K. Müller, *Ann.*, 1931, 490, 257; *Brit. Chem. Abs. A.*, 1931, 1427.

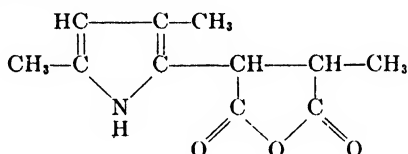
<sup>70</sup> O. Diels and K. Alder, with D. Winter, *Ann.*, 1931, 486, 211; *Brit. Chem. Abs. A.*, 1931, 849. Toward triphenylmethyl, however, pyrrole behaves as a diene. See J. B. Conant and B. F. Chow, *J.A.C.S.*, 1933, 55, 3475.

The assumption naturally follows that the formation of pyrrole-2,5-dipropionic acid arises by decarboxylation of an intermediate tetracarboxylic acid (analogous to 2-methylpyrrole-5-succinic acid) and the dilevulic acid, by the hydrolysis of pyrrole-2,5-dipropionic acid.

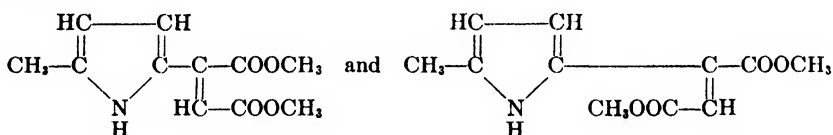


The 1-methylpyrrole-2,5-dipropionic acid is more resistant to hydrolysis, consequently the proportion of dilevulic acid is smaller.

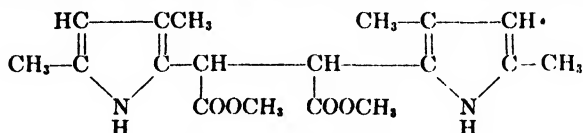
2,4-Dimethylpyrrole and citraconic anhydride in non-aqueous solvents react to yield a compound of the structure,



2-Methylpyrrole and methyl acetylenedicarboxylate combine additively at room temperature to yield stereoisomeric dimethyl esters which are cis- and trans-modifications inasmuch as they yield the same 2-methylpyrrole-succinic acid on catalytic reduction,



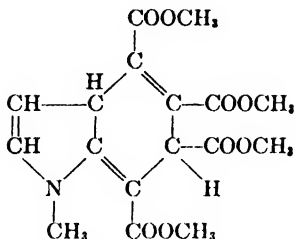
2,3-Dimethyl- and 2,3,4-trimethylpyrrole behave similarly to 2-methylpyrrole. 1-Methylpyrrole and acetylenedicarboxylic acid form 1-methylpyrrole-2-maleic acid. 2,4-Dimethylpyrrole, however, gives rise to a compound having two nitro-



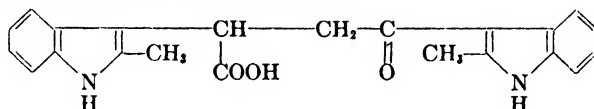
gen components. N-Methylindole behaves in the same manner. Methyl acetylenedicarboxylate, on the other hand, with 1-methylpyrrole reacts to give an indole of the structure<sup>71</sup>

<sup>71</sup> O. Diels, K. Alder and H. Winckler, *Ann.*, 1931, 490, 267, 276; *Brit. Chem. Abs. A*, 1931, 1428. O. Diels, K. Alder, H. Winckler and E. Petersen, *Ann.*, 1932, 498, 1; *Brit. Chem. Abs. A*, 1932, 1144. O. Diels and K. Alder, *German P.* 561,901, 1931, and 564,126, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1001, 1003.



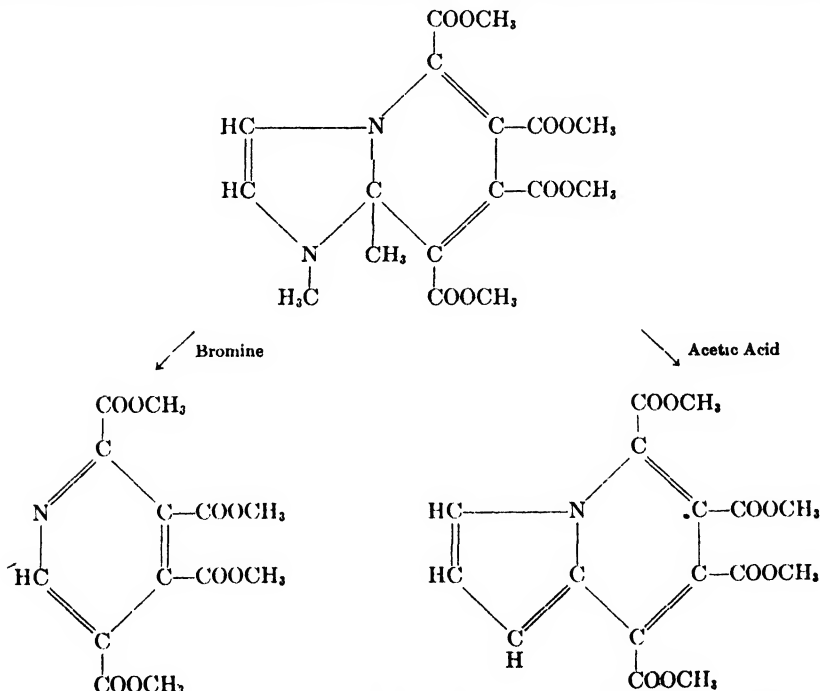


Maleic anhydride and 2-methylindole in benzene solution yield  $\alpha$ -2-methylindolyl-3-succinic anhydride and the compound,



With 1,2-dimethylindole and maleic anhydride similar compounds are obtained.<sup>72</sup>

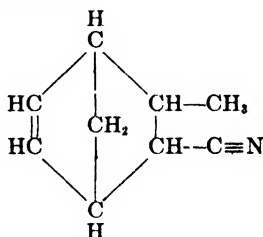
Methyl acetylenedicarboxylate and 4-methylglyoxaline in ether form methyl  $\alpha$ -4-methyl-2-glyoxalanyl-maleate. The 5-methylglyoxaline behaves in an analogous manner. Two mols of methyl acetylenedicarboxylate, however, combine with 1,2-dimethylglyoxaline in ethereal solution at room temperature to give an alizarin-red colored methyl 1,8-dimethyl-1,8-dihydropyriminazole-4,5,6,7-tetracarboxylate. This pyriminazole derivative, on treatment with bromine in methyl alcohol, is converted to methyl 2-methylpyridine-3,4,5,6-tetracarboxylate; with acetic acid, a loss of methylamine takes place and the resulting compound is an indolizine ester.



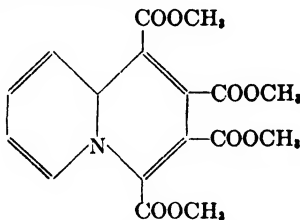
<sup>72</sup> O. Diels, K. Alder, U. Lübbert, H. Winckler, E. Heinrich, W. Lück and W. Eckhardt, *Ann.*, 1931, 490, 277; *Brit. Chem. Abs. A*, 1931, 1428.

The addition principle underlying the formation of the 1,8-dihydropyriminazole derivative is the addition of two mols of acetylenedicarboxylic ester to the  $=C=N-$  double bond.

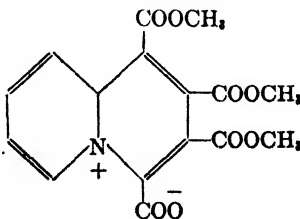
On the other hand,  $\alpha\beta$ -unsaturated nitriles react with dienes (cyclopentadiene, cyclohexadienes and butadienes) to form compounds retaining the nitrile group.<sup>75</sup> Thus crotonic acid nitrile adds to cyclopentadiene to yield 3-6-endomethylene- $\Delta^4$ -tetrahydro-1-methyl-2-cyanobenzene.



The principle<sup>76</sup> of addition to the  $=C=N-$  double bond is shown in the case of pyridine, quinoline and isoquinoline.<sup>77</sup> Pyridine and methyl acetylenedicarboxylate in ethereal solution yield tetramethyl quinolizine-1,2,3,4-tetracarboxylate which has been applied to a synthesis of conine, norlupinane and  $\psi$ -lupinine.<sup>78</sup> In addition to the quinolizine derivative, however, there are two other compounds formed when pyridine reacts with methyl acetylenedicarboxylate. The yellow quinolizine compound will pass over into a red modification; it is also formed initially in the reaction in very small amounts. There is a second red variety which is isomeric with the yellow quinolizine compound and which reverts into the yellow form on recrystallization. Diels, Alder<sup>77</sup> and collaborators have recently studied the constitution of these derivatives and assign the name tetramethyl quinolizine-1,2,3,4-tetracarboxylate to the yellow substance.



The red modification, also known as the "Kashimoto-body," is considered to be:



<sup>75</sup> British P. 341,047, 1928, to I. G. Farbenind., A.-G.; *Chem. Abs.*, 1931, 25, 4891.

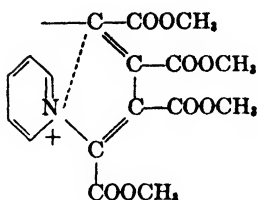
<sup>76</sup> O. Diels, K. Alder, H. Winckler and E. Petersen, *Ann.* 1932, 498, 1; *Brit. Chem. Abs. A*, 1932, 1144.

<sup>77</sup> O. Diels, K. Alder, T. Kashimoto, W. Friedrichsen, W. Eckhardt and H. Klare, *Ann.*, 1932, 498, 16; *Chem. Abs.*, 1932, 26, 5951.

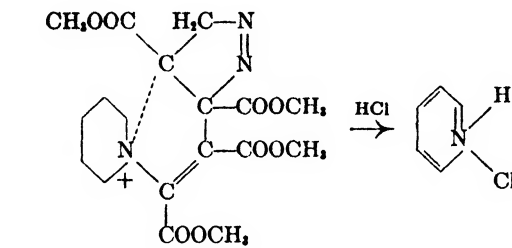
<sup>78</sup> O. Diels, K. Alder, W. Friedrichsen, H. Klare, H. Winckler and Schrum, *Ann.*, 1933, 505, 103; *Brit. Chem. Abs. A*, 1933, 1058.

<sup>77</sup> O. Diels, K. Alder, W. Friedrichsen, E. Petersen, Brodersen and Kech, *Ann.*, 1934, 510, 87; *Chem. Abs.*, 1934, 28, 5481.

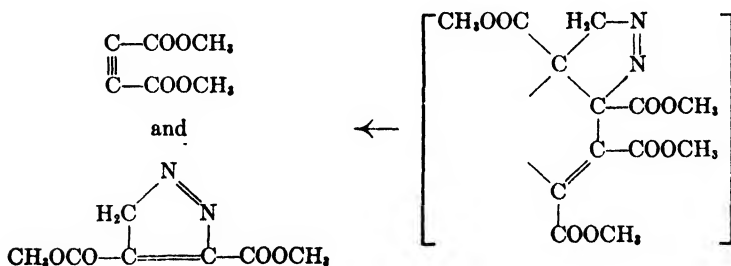
The isomeric red derivative known as the labile isomer is written as a pseudo-pyridinium structure,



This isomer is considered to be the intermediate in the quinolizine formation. The structure of this compound was obtained by treatment with diazomethane to form an adduct and splitting the resulting compound with hydrochloric acid into pyridine hydrochloride, dimethyl pyrazol-1,2,-dicarboxylate and dimethyl acetylenedicarboxylate.



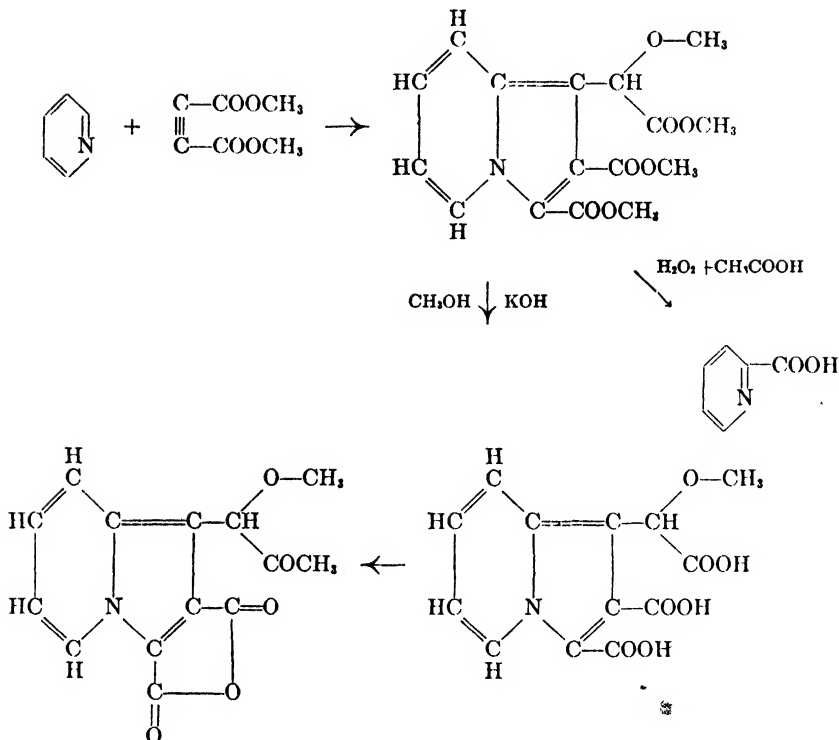
and



In a similar manner, quinoline and methyl acetylenedicarboxylate in benzene give a bright yellow addition product which is converted into a stable red isomer either by heating or by the action of concentrated sulphuric or hydrobromic acid. The quinoline derivatives behave in much the same manner as the pyridine compounds described above.

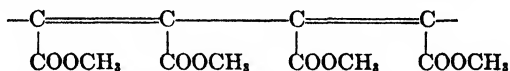
Diels and Meyer<sup>12</sup> have continued the study of compounds formed by reaction of pyridine and acetylenedicarboxylic acid esters. In methyl alcohol solution at 0°C. a colorless derivative is obtained which is known as the "white adduct" and which has been shown to be 1-( $\alpha$ -methoxy- $\alpha$ -carbmethoxy)-2,3-carbmethoxyindolizine. The "white adduct" on oxidation with hydrogen peroxide in acetic acid yields  $\alpha$ -picolinic acid; with alcoholic potash, hydrolysis occurs with the formation of 1-( $\alpha$ -methoxy- $\alpha$ -carboxy)-indolizine-2,3-carboxylic acid which is converted by boiling acetic anhydride into 1-( $\alpha$ -methoxy- $\alpha$ -acetyl)-indolizine-2,3-dicarboxylic anhydride.

<sup>12</sup> O. Diels and K. Meyer, *Ann.*, 1934, 513, 139; *Chem. Abs.*, 1935, 29, 1419.

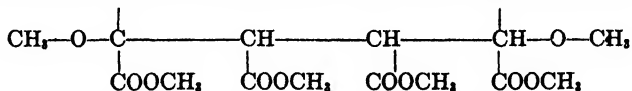


Reduction of 1-( $\alpha$ -methoxy- $\alpha$ -carboxy)-indolizine-2,3-dicarboxylic acid yields a resin which is converted with acetic anhydride into the tetrahydro derivative of 1-( $\alpha$ -methoxy- $\alpha$ -acetyl)-indolizine-2,3-dicarboxylic anhydride.

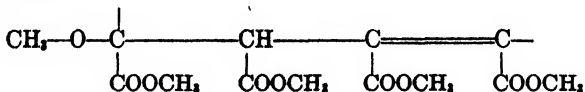
The mechanism of the addition of acetylenedicarboxylic acid esters to pyridine is not too well understood but the reaction has been explained in the following manner. Two molecules of the ester react to form an unsaturated chain



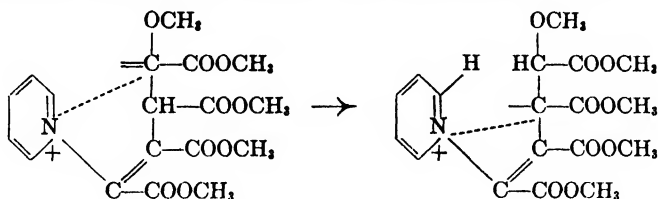
In ethereal solution the chain attaches itself to the nitrogen of the pyridine with the formation of quinolizine compounds. In methyl alcohol solution, however, 2 mols of alcohol could attach themselves to the unsaturated acetylene ester chain.



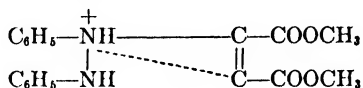
On fission 2 mols of methoxyfumaric ester should result. Credence to this hypothesis is substantiated by the isolation of methyl fumarate and methyl methoxyfumarate in the mother liquors in the preparation of the "white adduct." The addition of one molecule of methyl alcohol to the unsaturated ester chain would yield the following



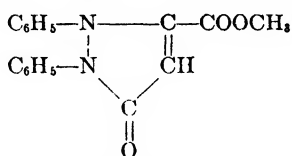
On the basis of the same type of addition as was noted in the formation of the pseudo-pyridinium structure, the reaction will take place as follows:



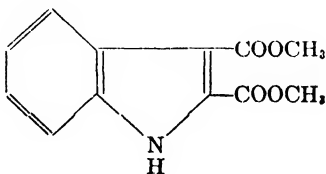
Diels and Reese<sup>79</sup> indicate that hydrazobenzene also forms an adduct with methyl acetylenedicarboxylate whose structure may be expressed as



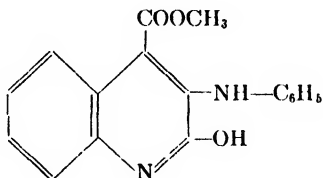
This compound may undergo a variety of reactions: by intramolecular loss of methyl alcohol, methyl 1,2-diphenylpyrazol-5-one-3-carboxylate is formed:



by loss of aniline, methyl- $\alpha,\beta$ -indole carboxylate,



and by loss of methyl alcohol and rearrangement, methyl 2-hydroxy-3-anilidoquinoline-4-carboxylate.

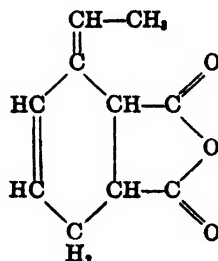


#### HEXATRIENES AND HIGHER POLYENES

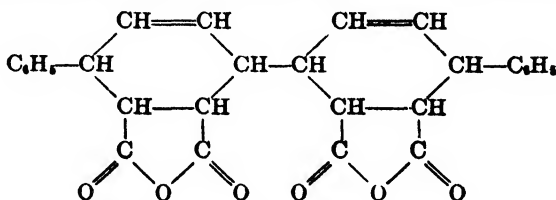
The hexatrienoids yield cyclohexene derivatives. Both the *cis* and the *trans* form of 1,3,5-hexatriene with maleic anhydride give rise to the same ethylidene cyclohexene derivative.<sup>80</sup>

<sup>79</sup> O. Diels and J. Reese, *Ann*, 1934, 511, 168; *Chem Abs*, 1934, 28, 5453

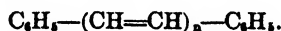
<sup>80</sup> E. H. Farmer and F. L. Warren, *J.C.S.*, 1929, 901.



1,8-Diphenyl-1,3,5,7-octatetraene unites with the same reagent to give the following:

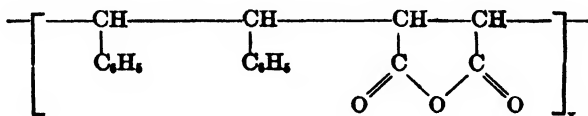


The reaction in this instance is probably dominated by the strong reactivity of the terminal methine groups. This seems to be true in the case of the higher hydrocarbons of the structure



1,10-Diphenyl-1,3,5,7,9-decapentaene reacts with either 2 or 3 mols of maleic anhydride. When 2 mols of the anhydride react, addition appears to take place in positions 1,4 and 7,10.<sup>22</sup>

By a so-called "additive heteropolymerization" maleic anhydride reacts with stilbene in boiling xylene solution to yield a compound of high molecular weight which is insoluble in most organic solvents and only colloiddally soluble with preliminary swelling in camphor. On dry distillation stilbene is regenerated. Wagner-Jauregg considers the structure to be according to a definite plan:



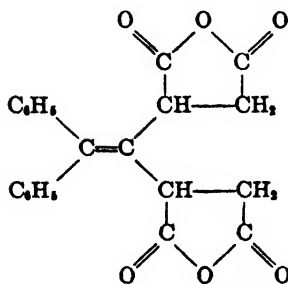
Amylene and styrene heated with maleic anhydride give viscous gummy masses.

The  $\text{C}=\text{N}$  union seems also capable of additive heteropolymerization, for with benzal- or cinnamal-azine, maleic anhydride reacts to form brown or yellow amorphous masses.<sup>23</sup> Asymmetrical diphenylethylene reacts with 2 mols of maleic anhydride to yield a crystalline derivative but when heated to  $330^\circ\text{C}$ . reverts partly to maleic anhydride and to unidentified resinous material. Wagner-Jauregg<sup>24</sup> considers this addition to be of the nature of the addition of maleic anhydride to pyrrole which does not involve a 1,4 addition. The structure would be, presumably:

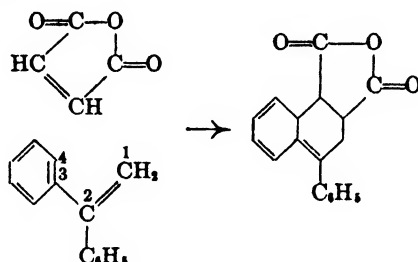
<sup>22</sup> R. Kuhn and T. Wagner-Jauregg, *Ber.*, 1930, 63, 2662; *Brit. Chem. Abs. A*, 1930, 1580.

<sup>23</sup> T. Wagner-Jauregg, *Ber.*, 1930, 63, 3213.

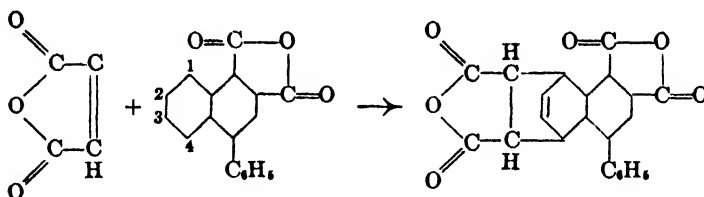
<sup>24</sup> T. Wagner-Jauregg, *Ann.*, 1931, 491, 1; *Chem. Abs.*, 1932, 26, 982.



Alder,<sup>24</sup> however, considers that one of the double bonds of the benzene ring acts as a conjugated system with the bond of the side chain. The first maleic anhydride acts on the system 1,4,



and the second maleic anhydride 1,4 on the second conjugate system in the benzene ring:



Certain types of reactions take place between monolefins and compounds containing the  $\alpha\beta$ -enal grouping. The structure of these derivatives has not been determined but they may be mentioned at this point. Olefins can be condensed with maleic acid, crotonic acid, acrylic acid, acrylic aldehyde or quinone. "Amylene succinic acid" has been prepared by heating amylene for 2 hours at 180°C. with 20 per cent by weight of maleic anhydride. The olefin aldehydes or carboxylic acids are useful in resin manufacture.<sup>25</sup>

Daimler<sup>26</sup> heated maleic acid with glycols such as 1,3-butylene glycol which are capable of splitting off water with the formation of unsaturated compounds. With 1,3-butylene glycol, the product is a syrupy liquid soluble in ammonium hydroxide. Maleic anhydride also reacts with castor oil and when this is combined with the product from maleic acid and 1,3-butylene glycol, an adhesive composition is obtained that is useful in safety glass manufacture.<sup>27</sup>

<sup>24</sup> K. Alder, "Methoden der Dien-synthese," *loc. cit.*, 3101. See Ref. 7, this chapter.

<sup>25</sup> French P. 743,503, 1933, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, 27, 3720. Dutch P. 32,029, 1934; *Chem. Abs.*, 1934, 28, 3745.

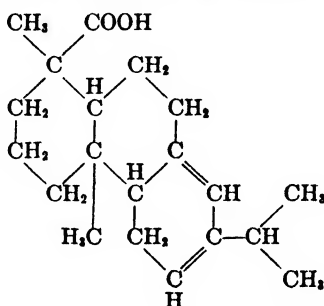
<sup>26</sup> K. Daimler, German P. 587,355, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 1404.

<sup>27</sup> K. Daimler and G. Balle, U. S. P. 1,904,671, Dec. 18, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 902. See Chapter 43.

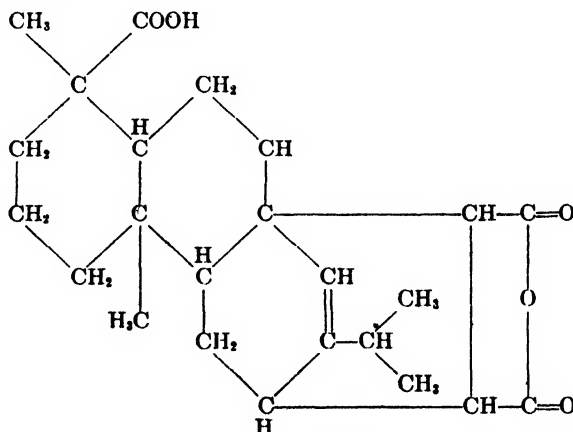
## ROSIN-MALEIC ANHYDRIDE ADDUCT

The diene synthesis, particularly the reaction with maleic anhydride, has thrown new light on the structure of abietic acid. The presence of two double bonds in abietic acid, but not their position is shown by hydrogenation. A dihydro-derivative is readily obtained but the tetrahydro with much more difficulty. Oxidation with perbenzoic acid likewise shows two double bonds.

Methyl abietate and maleic anhydride at 160°C. yield an additive compound of the formula  $C_{28}H_{44}O_5$  which on hydrolysis passes over into the anhydride carboxylic acid  $C_{28}H_{42}O_5$  (m.p. 227-8°C.). This same compound is obtained from American colophony by direct treatment with maleic anhydride. The fact that abietic acid and maleic anhydride react indicates that a diene system probably exists and the formula of abietic acid may be written<sup>28</sup> provisionally as:



Arbuzov<sup>29</sup> prepared the same compound of abietic acid and maleic anhydride,  $C_{28}H_{42}O_5$ , (m.p. 227°C.).



The adduct when heated with selenium to 300°C. yielded retene, which may also be obtained from abietic acid and heat directly. The natural assumption is that the maleic anhydride dissociates during the reaction. That this is not wholly the explanation is shown by the fact that abietic-maleic anhydride dissociates at 385-400°C. whereas retene is formed at 300°C.

Rosin reacts with maleic anhydride on heating. Other anhydrides (aconitic

<sup>28</sup> L. Rusicka, P. J. Ankersmit and B. Frank, *Helv. Chim. Acta*, 1932, 15, 1239; *Brit. Chem. Abs. A*, 1932, 1254. See also Chapter 37.

<sup>29</sup> B. Arbuzov, *J. Gen. Chem. U. S. S. R.*, 1932, 2, 806; *Chem. Abs.*, 1933, 27, 2683.



and citric) will also react. The resulting acids may be esterified with alcohols or with glycerol to yield resins.<sup>90</sup> The process may be applied to rosin, ester gums derived from rosin, phenol-formaldehyde resins modified with rosin, or alkyls modified with rosin. Other resins, such as dammar and gum mastic, may also be used.<sup>91</sup>

The quantity of unsaturated acid added varies from 5-35 per cent of the weight of unsaturated resin. Thus, 35 parts of maleic anhydride are introduced at 150°C. into 100 parts of American wood rosin. After 1.5 hours the product no longer gives the Storch-Morawski test for colophony, but forms a brown resin softening about 25°C. above the softening point of the initial rosin. By the use of 150 parts of colophony, a product is obtained which may be esterified with glycerol, yielding a resin softening at a higher temperature than rosin glycerol ester.

The condensation with the unsaturated acid may be effected in solution: 100 parts of colophony and 30 parts of maleic anhydride yield, on refluxing for 4.5 hours in o-dichlorobenzene a resin softening above 100°C. and having an iodine value of 63. On heating the products obtained according to these two methods at 250-350°C., either with or without addition of 5 per cent of zinc chloride, resins of low acid number are produced. All these resinous substances are soluble in alkali, and the solutions yield the corresponding heavy-metal resins on the addition of metallic salts. The method is particularly adaptable to the preparation of the corresponding lead carboxylate. If 33 parts of trihydroxystearic acid are heated *in vacuo* to 200°C. with 40 parts of the rosin-maleic adduct, a resin is produced having properties resembling those of shellac.

The products formed by condensation of maleic anhydride with a glycerol or sorbitol ester of rosin are not soluble in alkali, but dissolve in benzene. For the production of a varnish, an equal weight of linseed oil may be added to a resin formed by heating 100 parts of colophony with 35 parts of maleic anhydride at 150°C., the whole being heated for 5 hours at 250°C. Decrease in the proportion of maleic anhydride to 25 per cent by weight results in formation of a resin of higher softening point. According to Robertson,<sup>92</sup> linseed and bodied oils (slow drying) and the glycerol-maleic acid-rosin types of resin give good colors in paints formulated with titanium pigments.

The rosin-maleic-glycerides have been found to possess properties rendering them adaptable to the production of light-colored high-grade varnishes.<sup>93a</sup> One particular rosin-maleic-glyceride has an acid number below 28, and is soluble in hydrocarbon solvents, turpentine and drying oils, but insoluble in the lower aliphatic alcohols. As a baking enamel, the resin may be mixed with one and a half parts of linseed oil and heated as high as 90°C.; as an air-drying varnish, one part of resin may be used with three or four parts of drying oil. The pale color and light-fastness of the resin render it useful for light-tinted enamels or varnishes. Such varnishes have good insulating properties. Maleic rosin glyceride is compatible with nitrocellulose, although its greater hardness necessitates the use of larger amounts of plasticizers.

#### THE DIENE SYNTHESIS AND THE STRUCTURE OF DRYING OILS

Fokin<sup>93</sup> was apparently the first to suggest that conjugated double bonds existed in the tung-oil molecule. Recent researches based on the ozonolysis<sup>94</sup> of the com-

<sup>90</sup> British P. 355,281, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.* 1932, 72. French P. 711,924, 1931; *Chem. Abs.*, 1932, 26, 2072.

<sup>91</sup> British P. 399,206, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.* 1933, 1021.

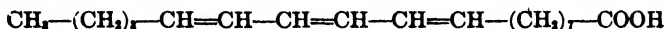
<sup>92</sup> D. W. Robertson, *Off. Digest Fed. Paint Varnish Prod. Clubs*, 1933, 126, 200; *Brit. Chem. Abs. B.* 1933, 1018.

<sup>93a</sup> Such a resin is that marketed under the trade name of "Resin K. M." by Messrs. Grindley & Co., Ltd., England.

<sup>94</sup> S. A. Fokin, *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 283; *J.C.S.*, 1913, 104(1), 442.

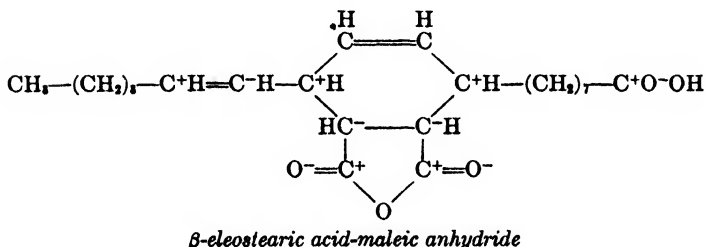
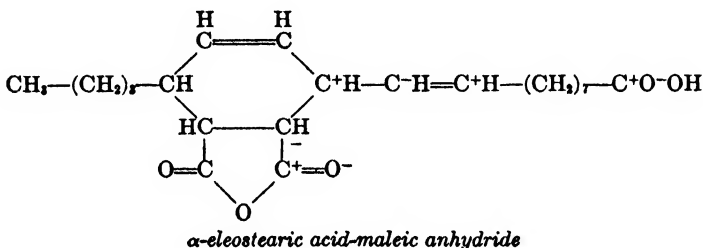
<sup>95</sup> A. Eibner and E. Rossmann, *Chem. Umschau, Fette, Oele, Wachse, Harze*, 1928, 35, 197; *Chem. Abs.*, 1928, 22, 4839. J. Böseken, *J.S.C.I.*, 1929, 48, 717. J. van Loon, *Farben-Ztg.*, 1930, 35, 1767; *Chem. Abs.*, 1930, 24, 4178.

pound have borne out this contention and the formula assigned to eleostearic acid is



Two reactions take place on halogenation. The first trace of halogen causes an isomeric change, the  $\alpha$ -eleostearic acid goes over into the  $\beta$ -variety inasmuch as the same crystalline hexabromide is obtained with either the  $\alpha$ - or  $\beta$ -form by halogenation in carbon tetrachloride in the presence of ultraviolet light. Debromination results in the regeneration of the  $\beta$ -eleostearic acid. Four atoms of bromine are taken up readily whereas the hexabromoeleostearic acid is formed slowly and in a poor yield.\*

Now, inasmuch as the eleostearic acids contain a system of double bonds, they should act as dienes with maleic anhydride to form a substituted, partially hydrogenated phthalic anhydride. This was found to be the case. Morrell and Samuels\*\* investigated this reaction between maleic anhydride and the  $\alpha$ - and  $\beta$ -eleostearic acids of tung oil. Both of these acids gave crystalline derivatives, the structures of which could be determined by oxidation with potassium permanganate and are



The structural formulas assigned above receive added support from surface-potential measurements. On dilute acid solution both the  $\alpha$ - and  $\beta$ -form spread to a unimolecular film with a limiting area of about 125 square Å per molecule. This is taken to mean that the molecules are flat on the surface and not end-on, as is ordinarily the case. The films of both the  $\alpha$ - and  $\beta$ -form behave similarly on compression down to an area of 100 square Å, whereupon for the  $\alpha$ -derivative the surface potential of the film falls from +280 to +80 m.v. on compression from 80-30 square Å; for the  $\beta$ -derivative under the same compression, the potential rises from +260 to +285 m.v.

This difference may be explained on the basis of alternating polarity. The magnitude of the polarity with respect to the maleic anhydride residue in each com-

\* J. Van Loon, *Rev. trav. chim.*, 1931, 50, 32; *Chem. Abs.*, 1931, 25, 2689.

\*\* R. S. Morrell and H. Samuels, *J.C.S.*, 1932, 2351. R. S. Morrell, S. Marks and H. Samuels, *J.S.C.I.*, 1933, 52, 130T.

pound will be the same but opposite in direction along the chain. On compression of the film from the state where the molecules are flat in the surface to the point where only the terminal group is in the surface, it follows that the 9,10-double bond (from the carboxyl) in the  $\alpha$ -compound is  $\pi$  when it is moved from the surface and when tending toward the vertical. This will oppose the  $\pm$  vertical component of the carboxyl group and tend to decrease the total vertical component of the electric moment per molecule much more than in the  $\beta$ -derivative where the electric moment of the 5,6-double bond (from the methyl group) is in the same sense as that of the carboxyl group on compression.

$\beta$ -Eleostearin-maleic anhydride differs from the  $\alpha$ -modification in that the solution can be stored at temperatures of 80-100°C. to give films which resist the action of cold alcohol, benzene and xylene. The  $\alpha$ -eleostearin films do not dry even after 8 hours heating and do not resist the action of benzene. This thermohardening property of the  $\beta$ -compound appears to be due to the oxidation of the double bond on the end remote from the glyceryl group. In the case of the  $\alpha$ -compound, steric hindrance is offered as a possible explanation for the retardation of oxidation.<sup>97</sup>

The  $\beta$ -eleostearin adduct with maleic anhydride is a pale yellow viscous mass, very readily soluble in acetone, alcohol, ether, benzene, turpentine and glacial acetic but only slightly soluble in 40-60°C. petroleum ether. When freshly prepared, it is miscible with linseed oil. Analytical figures showed the compound to be a triglyceryl ester of the formula  $C_{57}H_{102}(C_{22}H_{34}O_4)_3$ . A benzene solution of the product stored at 90-100°C. in 90 minutes to a hard colorless film which was elastic, non-webbing, non-frosting and non-blooming. The film may be dried at ordinary temperatures by use of cobalt linoleates or manganese resins. Neutralizing the acidity by further esterification or by the addition of lime increases the viscosity of the varnish.<sup>98</sup>

Adam and Morrell<sup>99</sup> have developed a method of measuring the water-attractive power of varnishes by determining the angle of contact between the film and water. This angle is determined to within 5° by tilting a flat plate until the water surface remains undistorted. With practically all of the varnishes, it was found that "blooming" accompanies a contact angle of less than 60°. If the angle is greater than 80°, the varnish does not bloom. The exceptions were those instances where the films dried slowly such as leaded drying oil. Stoving, which destroys blooming, increases the contact angle. In non-blooming varnishes which have angles from 80-100°, it appears as if all the oxygenated portions of the linoxyn molecules were covered by hydrocarbon residues through orientation.

The film-contact angles of some of the air-dried and some of the  $\beta$ -eleostearic-maleic anhydride films were found to bloom and have low contact angles whereas the very slow drying  $\alpha$ -films have high contact angles and show no bloom. Cobalt, manganese and lead-resinate driers have no apparent effect on the angle of contact or on the blooming of the films. Esterification of the  $\beta$ -derivative with either glycerol or glycol raises the contact angle and thereby diminishes the water-attractive power. It appears as if the greater exposure of the double bond in the  $\beta$ -compound might be responsible for the more rapid drying. Indications point to the fact that in the dried film the molecules tend to stand more or less perpendicular to the surface with the carboxyl end buried in the interior.<sup>100</sup>

At high temperatures (the so-called "stand-oil formation"), it has been sug-

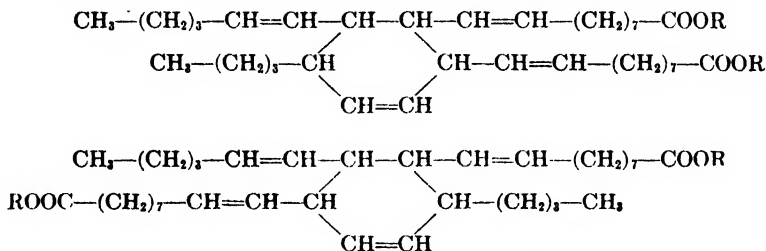
<sup>97</sup> A. H. Hughes (*J.C.S.*, 1933, 338), in a study of the surface films of  $\alpha$ - and of  $\beta$ -eleostearic acid-maleic anhydride, found that both acids undergo autoxidation in the unimolecular film but that this is completely inhibited by 0.12 per cent of quinol in the substrate.

<sup>98</sup> R. S. Morrell, S. Marks, and H. Samuels, *British P.* 407,987, 1932; *Brit. Chem. Abs. B*, 1934, 511.

<sup>99</sup> N. K. Adam and R. S. Morrell, *J.S.C.I.*, 1934, 53, 255T.

<sup>100</sup> N. K. Adam and R. S. Morrell, *J.S.C.I.*, 1934, 53, 360T.

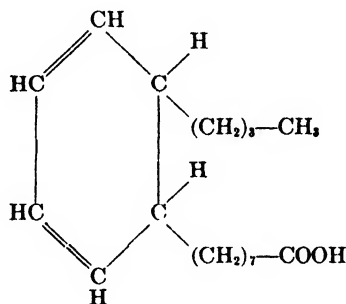
gested that the conjugated system of eleostearic acid may undergo a reaction analogous to the diene synthesis with the formation of high-molecular glycerides. The reaction would probably be pictured as:



It has also been speculated that linseed oil, at high temperatures, through isomerization may pass over into a diene system to undergo a similar intermolecular change. The transformation of linseed oil, however, is more complicated due to the fact that unpolymerized linseed oil also undergoes re-esterification.<sup>101</sup>

Jordan<sup>102</sup> is also of the opinion that in the first stages of polymerization of eleostearic acid there is a loss of one double linkage for each molecule of acid. He also proposed a **T** formula for the glycerides in place of the more usual **E** representation.<sup>103</sup> Using the **T** form it can be shown that combination can take place only by union of separate molecules.<sup>104</sup>

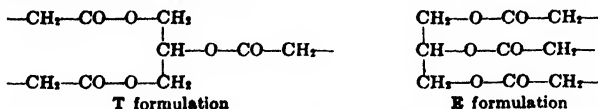
In a study of the eleostearic acids, Rossman<sup>105</sup> maintains that below 300°C. polymerization does not occur beyond the dimeric stage. Cyclomonoeleostearic acid (b.p. 200°C. at 4 mm.) is formed in variable amounts by heating  $\alpha$ - and  $\beta$ -eleostearic acids. Rossman believes it to be 2-butyl- $\Delta^{3,5}$ -cyclohexadienyl octoic acid



<sup>101</sup> C. A. P. Kappelmeier, *Farben-Ztg.*, 1933, 38, 1018, 1077; *Chem. Abs.*, 1933, 27, 4425. See also C. A. P. Kappelmeier, *Chemisch Weekblad*, 1934, 31, 423.

<sup>102</sup> L. A. Jordan, *J. Oil, Colour Chem. Assoc.*, 1934, 17, 47; *Brit. Chem. Abs. B*, 1934, 333.

<sup>103</sup> The **T** and **E** forms differ as follows:



On the basis of x-ray examination of the triglycerides from tridecain to tristearin, C. E. Clarkson and T. Malkin (*J.C.S.*, 1934, 666) conclude that the stable  $\beta$ -form, which possesses the higher melting point, has long carbon chains tilted across planes formed by terminal methyl groups. In the  $\alpha$ -form, the chains are considered to be perpendicular to these planes. They likewise favor a **T** formulation rather than an **E** for the triglycerides. For other x-ray examinations of long-chain esters see T. Malkin, *Trans. Faraday Soc.*, 1933, 29, 977; *Brit. Chem. Abs. A*, 1933, 1107. *J.C.S.*, 1931, 2796.

<sup>104</sup> L. A. Jordan and J. O. Cutter, *J.S.C.I.*, 1935, 54, 897. J. O. Cutter and L. A. Jordan, *J. Oil, Col. Chem. Assoc.*, 1935, 18, 5; *Chem. Abs.*, 1935, 29, 2762.

<sup>105</sup> E. Rossman, *Fettechem. Umschau*, 1933, 40, 961, 117; *Brit. Chem. Abs. A*, 1933, 807.

A cyclodieleostearic acid is reported to have been separated from tung oil that had been gelled and further heated at 290°C. for 0.5 hour.

In the heat-polymerization of the highly unsaturated fatty acids isolated from Japanese sardine oil, the following factors were noted: the iodine value falls, the specific gravity and refractive index rise, the specific viscosity rises rapidly. The acid and saponification values decrease, while the ester value increases. Extraction of the syrupy polymerization products with light petroleum yielded resinous substances. Toyama and Tsuchiya<sup>106</sup> consider that, in the first stages of polymerization, intramolecular change such as ring formation preponderates over extra-molecular polymerization.

Van Loon<sup>107</sup> has studied oiticica oil from the *Couepa grandiflora* or *Licania rigida* of Brazil; this oil contains "couepinic acid," an acid which is a geometrical isomeride of  $\alpha$ - and  $\beta$ -eleostearic acids. Po-yoak oil (from *Parnarium Sherbroesne*) is closely related to oiticica oil and may find use as a tung oil substitute.<sup>108</sup> The  $\beta$ -couepin of this oil reacts with maleic anhydride to yield a viscous syrup; it has not been reported to have given a fully thermohardening resin.<sup>109</sup>

CH,

Dehydrogeranic acid,  $(\text{CH}_2)_2=\text{CH}-\text{CH}=\text{CH}-\overset{\text{CH}_3}{\underset{|}{\text{C}}}=\text{CH}-\text{COOH}$ , from the wood of *Callitropsis araucarioides*, could not be condensed with maleic anhydride,<sup>110</sup> although structurally (from absorption spectrum analysis) the acid contains a conjugate system

<sup>106</sup> I. Y. Toyama and T. Tsuchiya, *Chem. Umschau*, 1929, **36**, 45; *Brit. Chem. Abs.* **B**, 1929, 291.

<sup>107</sup> J. van Loon, *Verf. kronach*, 1931, **4** (10), 7, 11; *Chem. Abs.*, 1932, **26**, 1463. See J. van Loon and A. Steger, *Rec. trav. chim.*, 1931, **50**, 936; *Brit. Chem. Abs.* **A**, 1931, 1034.

<sup>108</sup> J. van Loon, *Farben-Ztg.*, 1932, **37**, 483; *Brit. Chem. Abs.* **B**, 1932, 194. J. van Loon (*Z. Untersuch. Lebensm.*, 1930, **60**, 320; *Chem. Abs.*, 1931, **25**, 4727) discussed the thiocyanometry of tung oil and the possible existence of  $\gamma$ -eleostearic acid.

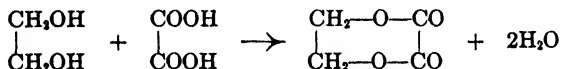
<sup>109</sup> See R. S. Morrell, S. Marks and H. Samuels, *British P.* 407,957, 1932; *Brit. Chem. Abs.* **B**, 1934, 511.

<sup>110</sup> R. S. Cahn, A. R. Penfold and J. L. Simonsen, *J. C. S.*, 1931, 3'34.

## Chapter 4I

### Polybasic Acid-Polyhydric Alcohol Resins. Alkyd Resins. Theoretical

The esterification of polybasic acids by polyhydric alcohols leads almost invariably to the formation of condensation products of high molecular weight. It is, indeed, only in a few cases—such as the esterification of ethylene glycol with carbonic or oxalic acid derivatives—that the simple monomeric ester is formed in other than a very small yield. This simple reaction may be represented as follows:

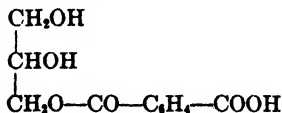


More usually, as was first noted by von Bemmelen<sup>1</sup> in the esterification of succinic acid,  $\text{HOOC—CH}_2\text{CH}_2\text{—COOH}$ , with glycerol,  $\text{HOCH}_2\text{—CHOH—CH}_2\text{OH}$ , the product is a vitreous, resin-like body.

The utilization of these polymeric compounds or resins was tardy, partly owing to their high cost but more particularly to a lack of recognition of their qualities and variety of uses. In recent years, however, phthalic anhydride, the anhydride of the simplest aromatic dibasic acid, has become a readily accessible industrial product used in the manufacture of dyestuffs. When this acid is combined with glycerol, a by-product of the soap industry, the so-called alkyd resins are obtained and these have acquired considerable industrial importance.

**Phthalic Glyceride.** Whenever an organic acid reacts with an alcohol the product is an ester. The reaction between phthalic anhydride (or acid) and glycerol is no exception to this rule, but the ester formed is of a complex nature, having a high molecular weight and resinous properties and thus differing greatly from ordinary esters. As is known, polybasic acids, reacting with monohydric alcohols, form simple esters, (diethyl phthalate from ethyl alcohol and phthalic anhydride). Moreover, polyhydric alcohol esters of monobasic acids are without complexity (triacetin and vegetable oils). The high degree of molecular complexity of the resinous esters formed when both components are poly-functional<sup>2</sup> can be explained if one considers the various ways in which combination is possible.

When phthalic anhydride and glycerol are heated the first product may be assumed to be the phthalic acid monoglyceride:



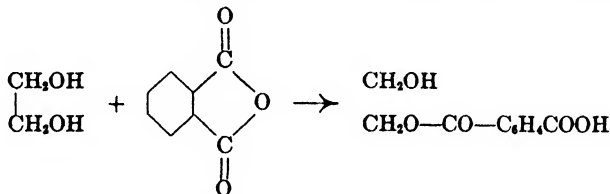
That this is not the final product is easily understood when it is noted that this compound is simultaneously both an acid and an alcohol. Further reaction is there-

<sup>1</sup> J. M. von Bemmelen, *J. prakt. Chem.*, 1856, (1) 69, 84; *Jahresber.*, 1856, 603.

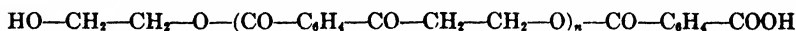
<sup>2</sup> See Chapter 4.

fore possible, leading to intermolecular esterification of the initial ester and forming finally immense resin molecules as an end-product.

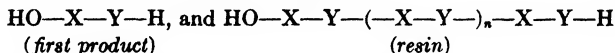
The structure of phthalic glyceride is difficult to picture graphically on account of the complexity of glycerol itself. But if glycol, which is simpler than glycerol, is the reacting polyhydric alcohol, the reaction is probably as follows:



The initial ester may then combine intermolecularly to form a long chain-molecule:



If HO-X-OH is glycol (or another dihydric alcohol) and H-Y-H is phthalic acid (or any dibasic acid), the symbolic formula is:



The symbolic formula for phthalic glyceride differs from that of the glycol resin in having a branch-chain at each glycerol residue since there are three hydroxyl groups in glycerol to enter the reaction and only two in glycol.

**Classification of Alkyd Resins.** As might be anticipated the general properties of such resins vary according to the type of acid and alcohol employed.\* Kienle and Ferguson<sup>4</sup> distinguish three main classes: (a) Resins non-convertible by heat, namely, those formed from dihydric alcohols (glycol) and dibasic acids (phthalic anhydride), which do not gel on heating. (b) Heat-convertible resins, given by alcohols with not less than three hydroxyl groups (glycerol) and dibasic acids, or by dihydric alcohols and acids with not less than three carboxyl groups. These resins, as first produced by esterification, are converted by further heat treatment into infusible and insoluble products. (c) Element-convertible resins, those derived from unsaturated acids or alcohols, the properties of which are irreversibly altered by the oxidation of the unsaturated component.

One theory of resin formation was suggested by Kienle and Hovey<sup>5</sup> and further elucidated by Kienle.<sup>6</sup> Whenever the reactivity of an organic reaction is 2 to 2 (e.g., glycol and phthalic anhydride), where there are two functional groups, an amorphous or resinous substance results unless, as Carothers<sup>7</sup> has shown, the monomer can form a 5- or 6-membered ring. In these special cases cyclization would tend to take place and crystalline compounds would result. Thus with ethylene glycol and oxalic acid, a monomeric ester is formed. With glycerol and phthalic anhydride, the reactivity is 3 to 2, respectively, that is, there are three functional groups in glycerol but only two in phthalic anhydride. The tendency under these

\* These resins are often called "Glyptals," an incomplete anagram derived from the words gly(cerol) and p(h)yt(h)al(ic). This term has been adopted by the General Electric Co. for alkyd resins.

Hönel feels that the designation "glyptal" should be restricted to resins which on sufficiently prolonged condensation yield infusible and insoluble products. Such resins may have phthalic anhydride replaced by other polybasic acids, and within certain limits dihydric alcohols and monobasic acids may be substituted to confer modified properties. When such limits are exceeded, however, infusible limit products are not formed, and the term "glyptal" should then no longer be used. See H. Hönel, *Paint, Oil, Chem. Rev.*, 1931, 91 (22), 19; *Chem. Abs.*, 1931, 25, 3854.

The use of the name alkyd avoids the introduction of trade names.

<sup>4</sup> R. H. Kienle and C. S. Ferguson, *Chem. Met. Eng.*, 1932, 39, 599.

<sup>5</sup> R. H. Kienle and A. G. Hovey, *J.A.C.S.*, 1929, 51, 509.

<sup>6</sup> R. H. Kienle, *Ind. Eng. Chem.*, 1930, 22, 590.

<sup>7</sup> W. H. Carothers, *Chem. Rev.*, 1931, 8, 353.

conditions would likewise be to form chains but these chains could react with one another to form a highly complex, 3-dimensional pattern yielding on heating a large molecule which was both infusible and insoluble. (See Table 41.)

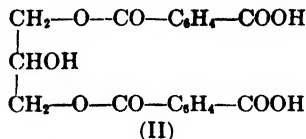
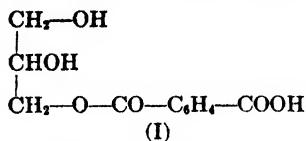
By the addition of monobasic acids to phthalic anhydride and glycerol, the course of the reaction is altered. The presence of the monobasic acid hinders the cross linkages of the chains. But with a highly unsaturated acid, cross linkages can occur through polymerization and oxidation of the side chains. This type of resin is known as the element- or oxygen-convertible type.\*

TABLE 41.—Effect of Varying Alcohols on Phthalic Anhydride.\*

Alcohol	Reactivity Acid/ Reactivity Alcohol	Type Resin
Methyl.....	2/1	No resin; pure compound.
Ethylene glycol.....	2/2	Heat-non-convertible. Hard glassy resin.
Propylene glycol.....	2/2	Heat-non-convertible. Hard resin.
Diethylene glycol.....	2/2	Heat-non-convertible. Balsam.
Glycerol.....	2/3	Heat-convertible. Hard glassy resin.
Mannitol.....	2/6	Heat-convertible. Hard opaque resin.

\* R. H. Kienle, *Ind. Eng. Chem.*, 1930, 22, 593

**Glycerol and Phthalic Anhydride.** The reaction between glycerol and phthalic anhydride since its discovery by Smith<sup>9</sup> in 1901 has been the subject of many investigations into the mechanism of resin formation. Kienle and Hovey,<sup>10</sup> in studying the rate of esterification of equivalent amounts of glycerol (2 mols) and phthalic anhydride (3 mols), found that reaction proceeded at first very rapidly, yielding within a minute, at the temperature investigated, a product corresponding to 50 per cent esterification, i.e., to a mixture of the monobasic mono-glyceride (I) and the dibasic diglyceride (II)



When esterification is about 60 to 70 per cent complete, the rate falls off, but proceeds more slowly up to and beyond the point at which gelation occurs. No aldehyde was detected in the reaction. This observation tends to invalidate the suggestion made by Barry, Drummond and Morrell,<sup>11</sup> that an intermediate aldehyde is the mechanism by which the alkyd resins are formed.

The preliminary formation of the monoesters was noted by Hönel,<sup>12</sup> who found that the continued heating of the infusible resin after gelation decreased its ability to swell with solvents, indicating the continuation of the process of esterification.

\* See Chapter 44.

<sup>9</sup> W. Smith, *J.S.C.I.*, 1901, 20, 1075.

<sup>10</sup> R. H. Kienle and A. G. Hovey, *J.A.C.S.*, 1929, 51, 509.

<sup>11</sup> T. H. Barry, A. A. Drummond and R. S. Morrell, "Natural and Synthetic Resins," D. Van Nostrand Co., New York, 1926. C. F. Peterson (British P. 250,949, 1926, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1926, 988) found that the addition of small quantities of phenol-formaldehyde resin to the alkyd resin had a tendency to accelerate the polymerization of the latter. This observation tends to support the view that acrolein might be an intermediate form. The fact that the formation of the alkyd resin occurs more readily with polyglycerols than glycerol itself may indicate that the polymerization of the glycerol itself is involved in some manner. See T. H. Barry, *Ind. Chemist*, 1928, 4, 53; *Chem. Abs.*, 1928, 22, 2071.

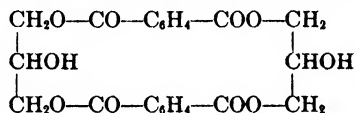
<sup>12</sup> H. Hönel, *Kunststoffe*, 1931, 35, 76, 105, 123; *Chem. Abs.*, 1931, 25, 5047.



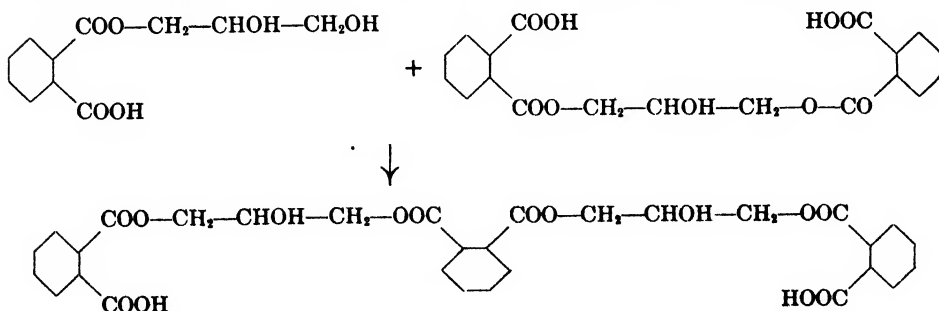
He therefore attributed resinification to the formation of compounds of high molecular weight solely by continued esterification of the acid esters first formed. Increase of the amount of glycerol causes the acid number of the mixture, immediately before it becomes infusible and insoluble, to decrease until finally the infusible state cannot be reached. When glycerol and phthalic anhydride are taken in such proportions as to form the mono- or the diester and heated, the reaction proceeds very slowly at 160°C. Above 230°C., the reaction is more rapid, but the tendency is to form hard resins. The greater the amount of phthalic anhydride, the greater is the tendency toward insolubility.<sup>13</sup>

Bozza,<sup>14</sup> on the other hand, regards the reaction as leading first to the esterification of the  $\alpha$ -hydroxyl groups of the glycerol, followed by a condensation process in which the molecular weight increases without increase in the degree of esterification, due to anhydride formation between the free acidic groups of adjacent molecules. Schlenker,<sup>15</sup> however, views the resins as long chains of glycerol molecules linked at the  $\alpha$ -positions through the carboxyl groups of alternating phthalic acid molecules, while the  $\beta$ -hydroxyl groups are esterified only in the later stages of the reaction.

Savard and Diner<sup>16</sup> made an extensive investigation of the kinetics of the esterification in question, and from the velocity constants of the process deduced that the initial step is the formation of the dibasic diglyceride already mentioned. This reacts with any excess of glycerol to form a neutral glyceride,



corresponding perhaps to conditions where an infusible resin cannot be formed. With excess of phthalic anhydride, the diglyceride reacts further at the  $\beta$ -hydroxyl group. In the absence of excess of either constituent, it is deduced that the diglyceride undergoes internal esterification. According to Hönel<sup>17</sup> it is this internal esterification that is responsible for the formation and the characteristic properties of the alkyd resins. He regards the first stage as giving rise (in equivalent mixtures) to a mixture of the mono- and diglycerides referred to above. With further heating, these react to give the condensation product as follows:



In the latter substance, two mols of glycerol are united to three mols of phthalic acid. The  $\beta$ -hydroxyl groups of the glycerol are still unesterified (corresponding

<sup>13</sup> S. Sugimoto, *Repts. Imp. Ind. Research Inst., Osaka, Japan*, 1932, 14 (13), 1; *Chem. Abs.*, 1934, 28, 4921.

<sup>14</sup> G. Bozza, *Giorn. chim. ind. applicata*, 1933, 14, 394, 400; *Chem. Abs.*, 1933, 26, 6162.

<sup>15</sup> E. Schlenker, *Allgem. Oel- u. Fett-Ztg.*, 1933, 29, 658; *Brit. Chem. Abs. B*, 1933, 187.

<sup>16</sup> J. Savard and S. Diner, *Bull. soc. chim.*, 1932, 51, 597; *Chem. Abs.*, 1932, 26, 5037.

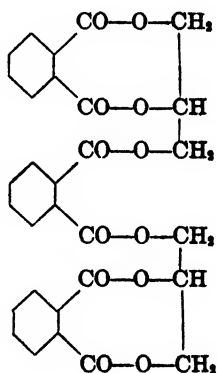
<sup>17</sup> H. Hönel, *loc. cit.*, 19.

to the invariable rule that the  $\alpha$ -hydroxyl undergoes reactions first),<sup>12</sup> one-third of the acidity of the phthalic anhydride remaining unneutralized. This stage of the reaction corresponds to the absence of excess of either component, and to the experimentally found change in the rate of esterification when 33 1/3 per cent free acid remains. The theoretical relationship between molecular weight and acid number,<sup>13</sup> representing various stages in the esterification of phthalic anhydride and glycerol, is shown below, where P represents phthalic acid and G, glycerol. A terminal P implies the presence of a carboxyl group and a terminal G, a dihydroxy group.

Table 41a.—*Theoretical Relationship between Molecular Weight and Acid Number in Glycerol-Phthalic Anhydride Esters.*

Name	Type Formula	Molecular Weight	Acid Number
Monoglycerol monophthalate	G—P	240	233
Diglycerol diphthalate	G—P—G—P	462	121
Triglycerol triphthalate	G—P—G—P—G—P	684	82
Tetraglycerol tetraphthalate	G—P—G—P—G—P—G—P	906	62
Monoglycerol diphthalate	P—G—P	388	280
Diglycerol triphthalate	P—G—P—G—P	610	184
Triglycerol tetraphthalate	P—G—P—G—P—G—P	832	135
Tetraglycerol pentaphthalate	P—G—P—G—P—G—P—G—P	1054	106

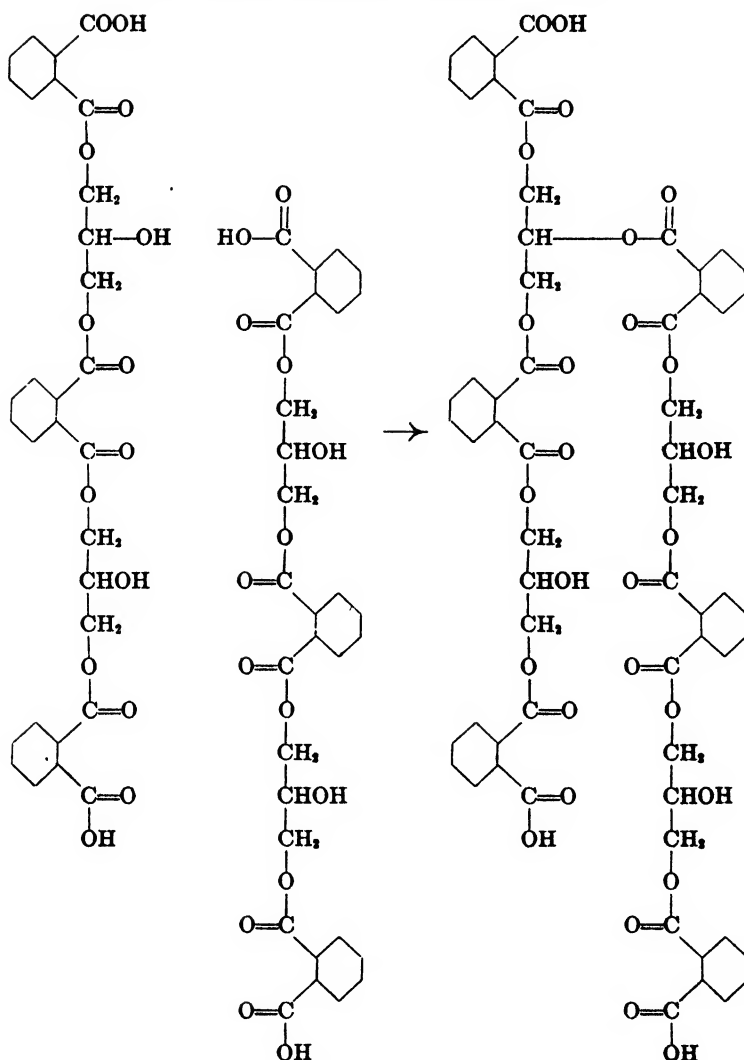
Further esterification, now involving the  $\beta$ -hydroxyl groups, might conceivably proceed internally, forming such a glyceride<sup>14a</sup> as



This is, however, unlikely, as the limit product is almost completely soluble in very dilute potassium hydroxide, requiring in fact, only as much alkali as is required to neutralize the free acid. The progressive decrease in acidity and corresponding increase in resin-like properties can, however, be far more readily explained by the esterification of a hydroxyl group by the acid of another molecule thus:

<sup>12</sup> Cf. A. Fairbourne and G. W. Cowdrey, *J.C.S.*, 1929, 139.

<sup>14a</sup> This is a hypothetical formula. According to E. W. Spanagel and W. H. Carothers (*J.A.C.S.*, 1936, 57, 299), cyclic esters involving 8-membered rings have never been prepared. Although it is a relatively simple matter to obtain cyclic polybasic acid-polyhydric alcohol esters in a monomeric form when the ring consists of 6 atoms (e.g., glycol oxalate) and also when the ring consists of a large number of atoms, the monomers corresponding to rings of 7 or 8 atoms are practically impossible to form.



By the continuation of the above process, formation of giant molecules may be visualized, consisting of long-branched chains of the type shown, which may perhaps further condense to ring structures of a high order. The length of such chains, and the corresponding colloidal properties of the resin, thus depend primarily on the length to which the heat treatment is carried beyond the point at which internal esterification commences.

Kienle and Race<sup>20</sup> studied the change in the electrical, chemical and physical properties of the modified and unmodified alkyd resins by measuring the changes in the D.C. resistance of the melts held at 190-195°C. During the formation of the unmodified alkyds there is a progressive increase in the electrical resistance with time (see Fig. 124). It may be seen that the further away the resin is from

<sup>20</sup> R. H. Kienle and H. H. Race, *Trans. Electrochem. Soc.*, 1934, 65, 231; *Brit. Chem. Abs. B*, 1934, 811.

the heat-convertible, the more the curve shifts to the right indicating higher resistance values for the same percentage of esterification. Inasmuch as the per cent esterification gives the number of carboxyl and hydroxyl groups, the higher resistance must be due to a factor other than ionization. Kienle and Race ascribe this to fluidity or mobility. For a given per cent esterification the shift from the heat-non-convertible (mobile) to the heat-convertible (less mobile) is accompanied by an increase in resistance. On this basis glycol phthalate gives a lower resistance than glycerol phthalate. Glycol phthalate, which produces a chain molecule rather than a criss-cross, three-dimensional molecule, readily approaches complete esterification without gelation and with a very high value for the resistance.

No simple or adequate explanation may be advanced to correlate the electrical characteristics. Debye's<sup>20</sup> theory of polar orientation, although mathematically

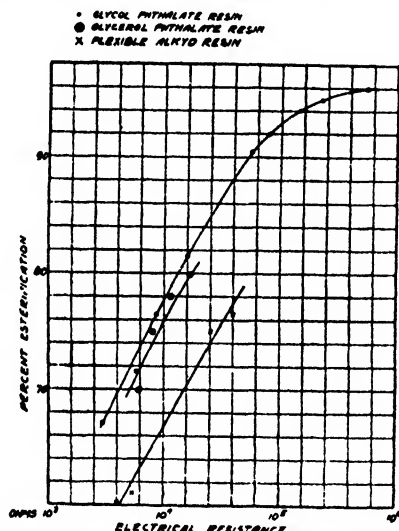


FIG. 124.—Comparison Between Per Cent Esterification and Electrical Resistance of Typical Alkyd Resins During Formation. (R. H. Kienle and H. H. Race.)

rigid only for dilute solutions, may be a contributing factor in both the heat-non-convertible resins and in the heat-convertible types at high temperatures. For the latter, however, it seems more probable that during gelation a cellular structure is formed of good insulating properties containing pockets of liquid or plastic semi-conductors.

A similar conclusion has been reached by Winning and Williams<sup>21</sup> from a study of the adsorptive properties of alkyd resins and the effect of curing. Their results agree with the assumption of giant molecules as the fundamental structural units, which increase in size and compactness, the chains lengthening and ramifying during the curing process, thereby decreasing the pore space and the adsorptive power. Corresponding to the decrease in adsorptive properties is a decrease in the tendency to disperse in a solvent, although as the pores take up solvent the resin swells, and can retain much solvent or vapor. The formation of ramified irregular chains is probably a characteristic property of the heat-convertible alkyd resins.

<sup>20</sup> P. Debye, "Polar Molecules," Chem. Catalog Co., New York, 1929.

<sup>21</sup> C. H. Winning and J. W. Williams, *J. Phys. Chem.*, 1932, 36, 3915; *Chem. Abs.*, 1932, 27, 651; *J.A.C.S.*, 1932, 55, 2560.

Wornum,<sup>22</sup> on the other hand, emphasizes the physical features. Two separate aspects must be considered in the colloidal behavior of ethylene glycol- and glycerol-phthalic anhydride: first, in the building up of the micelles and also the larger or secondary flocculates and, second, in the spatial distribution of the units throughout the system. The latter bears a distinct relation to phase stability which determines, among other things, the sol-gel transformation.

In a system such as ethylene glycol-phthalic anhydride, Wornum believes that the formation of larger units of the dispersed phase can only be accomplished through the operation of secondary valence forces. At high temperatures and in the absence of these valence forces, any aggregate must of necessity be of an evanescent character and, therefore, no gelation occurs. At lower temperatures these valence forces would become active, the micelles and secondary flocculates would then assume a more stable form resulting in a state of reversible gelation.

In the case of phthalic anhydride and glycerol, the conditions are less simple. The secondary valence forces act both at high and at low temperatures but, in addition, at higher temperatures it is necessary to consider the primary valence forces. Under these conditions larger units would easily be built up and the formation of irreversible micelles and irreversible flocculates would lead to irreversible gelation.

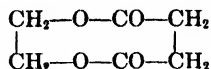
By means of specific-viscosity determinations<sup>23</sup> Houwink and Klaasens<sup>24</sup> have tested the concept that at temperatures below 180°C. only the  $\alpha$ -hydroxyl groups of the glycerol are active. At higher temperatures, the  $\beta$ -hydroxyl group enters into the reaction with the formation of a 3-dimensional polymer.

**Glycol Resins.** The esterification of glycol and other dihydric alcohols by dibasic acids, like the esterification of glycerol, leads to the formation of highly polymerized resinous products. The glycol resins differ however from the glycerol resins in that, even when esterification is carried to the limit, an infusible product is not formed. The glycol resins represent, then, the heat-non-convertible resins of Kienle and Ferguson.<sup>25</sup>

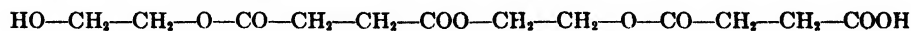
Taking the case of ethylene glycol and succinic acid as an example the first product of esterification will be the monoester.



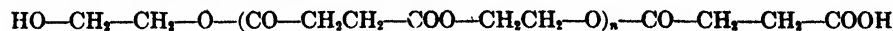
This might, according to circumstances, either undergo internal esterification, giving the neutral, monomeric ester



or else the free acid groups may esterify the free hydroxyl of another molecule, resulting in an acidic dimeric ester.



The first reaction leading to cyclization is excluded on the basis of the rule of Carothers;<sup>26</sup> consequently the intermolecular reaction would be expected. The process may thus be considered to proceed almost indefinitely, with the formation of linear polyesters of the general type:



in which the long chain-like molecule may be built out of many units. As may be

<sup>22</sup> W. E. Wornum, *Chem. Age (London)*, 1934, 30, 245. See Chapters 3 and 4.

<sup>23</sup> See Chapter 4.

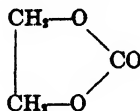
<sup>24</sup> R. Houwink and K. H. Klaasens, *Kolloid.-Z.*, 1935, 70, 329.

<sup>25</sup> R. H. Kienle and C. S. Ferguson, *loc. cit.*

<sup>26</sup> W. H. Carothers, *loc. cit.*

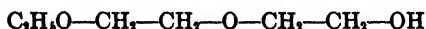
seen, the linear polymer differs distinctively from the extensively branched chains of the glycerol phthalate type. To this difference in structure of the final resin may be attributed variations in physical properties such as the gelation of the glycerol resins to an infusible product and the usual absence of such a property on the part of the glycol resins.

**Glycol and Carbonic Acid.** The neutral ester of glycol with carbonic acid, ethylene carbonate, is the 5-membered cyclic compound



As might be anticipated from the stereochemistry of 5-membered rings, the tendency is, therefore, toward cyclization to the simple ester rather than toward polymerization to resins. This is, in fact, the case;<sup>27</sup> ethylene carbonate is formed in good yield either by the action of carbonyl chloride (COCl<sub>2</sub>) or of 1 mol of chloroformic ester on ethylene glycol. In the latter case, the carbethoxy-glycol first formed eliminates alcohol intramolecularly, rather than intermolecularly, which would lead to polymerization.

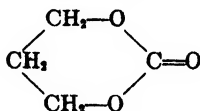
The carbonates of the glycol monoethers, and especially of diethylene glycol ether,



are high-boiling liquids which have been suggested as possible lacquer plasticizers.<sup>28</sup>

While ethylene glycol yields with carbonic acid only the monoester, polyesters may be obtained from other dihydric alcohols, all corresponding in composition to chains made up of the unit  $-\text{O}-(\text{CH}_2)_x-\text{O}-\text{CO}-$  which may recur 8 to 22 times.

Trimethylene carbonate exists both as the monomeric ester (m.p. 48°C.),



and as a glass of 38 to 45 structural units. Polymerization takes place on heating and is catalyzed by a trace of potassium carbonate. The glassy polymer is found by x-ray examination to be crystalline.<sup>29</sup>

By heating the linear polyesters with catalysts<sup>30</sup> it is possible in certain cases to bring about a smooth depolymerization to the monomeric or dimeric esters. The ratio of the monomer to the dimer is determined first on the nature of the ester, that is, its unit length and secondly on the experimental conditions.

Tetramethylene carbonate gives rise to a considerable amount of tetrahydrofuran, arising undoubtedly by the loss of carbon dioxide from the structural unit. The chief product was a 14-membered ring, a dimer which has been prepared by Ruzicka.<sup>31</sup> Carbonates of penta-, hexa-, hepta-, octa- and nonamethylene were chiefly dimeric. Decamethylene carbonate, however, yielded a considerable amount of monomer, the same being true of undecamethylene carbonate.<sup>32</sup>

<sup>27</sup> C. F. Alpress and W. Maw, *J.C.S.*, 1924, 125, 2359.

<sup>28</sup> N. O. Drake and R. M. Carter, *J.A.C.S.*, 1930, 52, 3750.

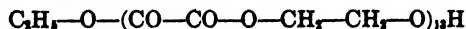
<sup>29</sup> W. H. Carothers and F. J. Van Natta, *J.A.C.S.*, 1930, 52, 323. W. H. Carothers, U.S.P. 1,995,291, Mar. 26, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 2975.

<sup>30</sup> J. W. Hill and W. H. Carothers, *J.A.C.S.*, 1933, 55, 5031.

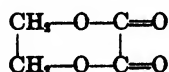
<sup>31</sup> L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1923, 11, 1159; *Chem. Abs.*, 1929, 23, 1110.

<sup>32</sup> J. W. Hill and W. H. Carothers, *J.A.C.S.*, 1933, 55, 5031.

**Glycol and Oxalic Acid.** The six-membered cyclic ethylene oxalate forms an intermediate stage between simple and polyesters. By the action of ethylene glycol on ethyl oxalate,<sup>33</sup> there is obtained a white powdery polymeric product, which from analyses and molecular weight determinations appears to be approximately of the composition

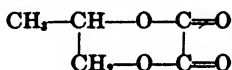


On heating the polymer in a vacuum, the monomeric ethylene oxalate, (m.p. 143°C.)



is formed in 50 per cent yield, but the solid substance undergoes polymerization in the course of a few days, being finally transformed into an insoluble form (m.p. 170-173°C.), in which it is possible to distinguish two polymers: one of m.p. 159°C. representing about 20-fold polymerization, the other probably higher.

Propylene glycol forms with ethyl oxalate a colored viscous resin from which, on heating in vacuum, monomeric propylene oxalate



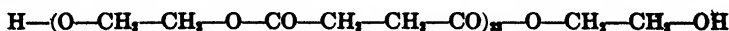
was obtained. This did not polymerize at the ordinary temperature, but could be converted at 140°C. to a completely insoluble polymer melting at 176-178°C.

Cyclization would not be anticipated in the reaction between trimethylene glycol ( $\text{HO—CH}_2\text{—CH}_2\text{—CH}_2\text{OH}$ ) and ethyl oxalate inasmuch as this would necessitate the formation of a seven-membered ring. The reaction takes place intermolecularly yielding a product of molecular weight of about 2000, i.e., a 15-20 structural-unit polymer. On distillation a small amount of dimer,



is formed.<sup>34</sup> Hexamethylene glycol and decamethylene glycol also give rise to linear polymers of the same type.

**Glycol and Succinic Acid.** By the action of succinic acid on excess glycol at 180°C., and subsequent removal of the excess glycol, a polymeric crystalline neutral glycol succinate is formed,<sup>35</sup> (m.p. 102°C.), which may be taken as typical of the glycol esters of dibasic acids. This substance may be represented by the formula,



consisting of 23 of the simple structural units,



linked together.<sup>36</sup> In the presence of excess of succinic acid, and with shorter times of heating there is a tendency to the formation of less-highly condensed, lower-melting products. Substances containing 6, 9, and 12 of the basic structural units in the molecule were thus obtained. In all cases, even with 2 mols of succinic acid per mol of glycol, high-molecular products were formed, and not the diacid ester,



<sup>33</sup> W. H. Carothers, J. A. Arvin and G. L. Dorough, *J.A.C.S.*, 1930, 52, 3393.

<sup>34</sup> W. H. Carothers, J. A. Arvin and G. L. Dorough, *loc. cit.*

<sup>35</sup> W. H. Carothers and G. L. Dorough, *J.A.C.S.*, 1930, 52, 711.

<sup>36</sup> The preparation of glycol esters of dibasic acids is also described by F. B. Sherland, *J.A.C.S.*, 1935, 57, 115.

The compound,  $\text{HO}-(\text{CH}_2)_2\text{O}-\text{CO}-(\text{CH}_2)_4-\text{CO}-\text{O}(\text{CH}_2)_2\text{OH}$ , formed as a viscous, non-volatile liquid by heating neutral ethylene succinate with glycol, is reconverted into the neutral ester and glycol on slow heating in vacuum.

These neutral ethylene succinates when dissolved in chloroform and spread on 0.01 *N* hydrochloric acid form stable unimolecular films. The molecular chains, so formed, are flexible and may be packed closely before disruption by compression.<sup>37</sup>

That esterification continues progressively, with the formation of longer, more-highly polymerized molecules, on continued heating, is indicated by Kienle and Hovey's<sup>38</sup> study of the rate of esterification of glycol with phthalic anhydride. As in the case of glycerol, rapid initial esterification was followed by a slower steady decrease in the free acidity, but no irreversible gelation occurred, the flow point and viscosity rising with time to final steady values indicating completion. Hönel<sup>39</sup> states that the monoester,  $\text{HO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{COOH}$ , corresponding to the initial rapid esterification, can be isolated.

**Properties of the Polymethylene Polyesters.** The esters of dibasic acids with dihydric alcohols are thus regarded in every instance as linear polymers. Carothers and Dorough<sup>40</sup> found that in all cases the limiting length of chain, under ordinary conditions, was about 200 atoms. Although diethylene glycol carbonate,

$\text{O}(\text{CH}_2)_2-\text{O}-(\text{CH}_2)_2-\text{O}-\text{C}=\text{O}$ , ethylene malonate and decamethylene phthalate are liquids, most of the esters are found by x-ray methods to be microcrystalline solids.

The physical properties of the substances depend largely on the nature of the structural units of which they are composed. Increase in the length of the polymethylene chains,  $-(\text{CH}_2)_n-$ , increases the solubility in organic solvents and diminishes the viscosity of the molten ester although this is always relatively high.<sup>41</sup> Where the ester groups are separated by polymethylene chains the substances may be crystalline. Less symmetrical polyesters, such as glycol phthalate, are resins (either transparent glasses or balsams). The crystalline esters also, when melted and cooled, yield opaque masses, which may be brittle and porcelain-like or soft and waxy. The waxy quality increases with the length of the polymethylene chains.

A special polyester found by Carothers and Van Natta<sup>42</sup> to possess toughness and elasticity was hexamethylene carbonate, which, though crystalline, separates from solution as opaque horny flakes. The reason for this property in hexamethylene carbonate alone is obscure.

As stated above, under normal working conditions the limit of condensation is a resin with a molecular weight of about 3000. Carothers and Hill<sup>43</sup> noted that by continuing the heat treatment in high vacuum, the so-called molecular still, the process could be carried further, yielding "super-polyesters" of modified properties. The properties of the products thus obtained may be exemplified by the polyethylene succinate so formed, which forms a tough, slightly elastic, horny mass at 97°, but flows only at a higher temperature. The melt may be drawn out into strong, pliable fibers; several of the esters, indeed, notably ethylene sebacate and the ester produced by auto-condensation of  $\omega$ -hydroxypentadecanoic acid, can be cold-drawn. It is not possible to spin filaments from the polyester of hydroxy-decanoic acid unless the molecular weight reaches about 7000. Cold drawing does not appear until the molecular weight approaches 9000. This relation between

<sup>37</sup> S. A. Moss, *J.A.C.S.*, 1934, 56, 41.

<sup>38</sup> R. H. Kienle and A. G. Hovey, *J.A.C.S.*, 1930, 52, 3636.

<sup>39</sup> H. Hönel, *Kunststoffe*, 1931, 35, 76, 105, 132; *Chem. Abs.*, 1931, 25, 5047.

<sup>40</sup> W. H. Carothers and G. L. Dorough, *J.A.C.S.*, 1930, 52, 717.

<sup>41</sup> W. H. Carothers and F. J. Van Natta, *J.A.C.S.*, 1930, 52, 317.

<sup>42</sup> W. H. Carothers and F. J. Van Natta, *ibid.*, 1930, 52, 314.

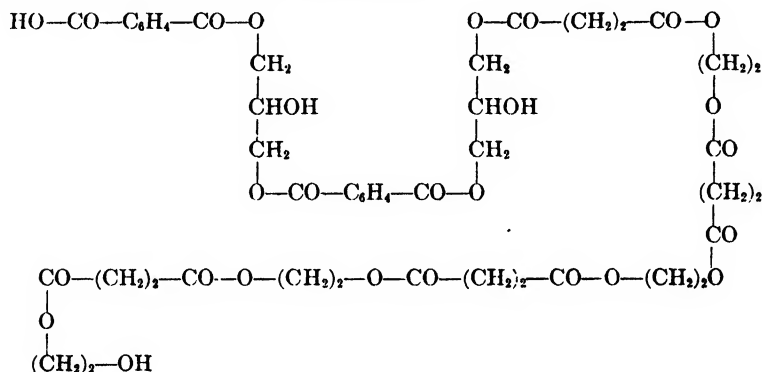
<sup>43</sup> W. H. Carothers and J. W. Hill, *ibid.*, 1932, 54, 1559.



the fiber and molecular length is important when it is seen that a fiber appears to require a molecule whose weight is at least 12,000 and whose length is not less than 1000 Å.

The glycol-phthalate resins also belong to this class of derivatives and have been proposed<sup>44</sup> in the production of artificial silk but, though lustrous threads may be obtained, they are exceedingly fragile according to Carothers and Hill.<sup>45</sup>

**Resins of Mixed Type.** Resins of the ethylene succinate type have been seen to possess the long-chain molecular structure favorable to the formation of flexible fibers; but to be non-heat-convertible. Kienle and Schlingman<sup>46</sup> have described heat-convertible flexible resins formed by introducing a proportion of the rigid, heat-convertible glycerol-phthalate into ethylene succinate. The resulting resins therefore comprise flexible, two-dimensional chains of the ethylene succinate type, which may be pictured as follows:



The resins are convertible by heat owing to cross-tying occurring between the glycerol phthalate units. The flexibility and hardness of the resins formed depend on the proportion of the two types present, increase in either the proportion or the chain length of the dihydric alcohol-dibasic acid component increasing the flexibility.

TABLE 42.—Properties of a Series of Flexible Alkyd Resins.\*

Mol per cent Glyceryl phthalate	Glycol succinate	Mol ratio	Flow point at "A" stage °C.	Cured resin Shore hardness	Shore elasticity
100	0		120		
50	50	1:1	123	99	—
33	67	2:1	67	97	—
20	80	4:1	55	95	33
14.3	85.7	6:1	50	83	38
11.2	88.8	8:1	60	63	95
9.1	90.9	10:1	55	55	95
0	100				

\* R. H. Kienle and P. F. Schlingman, *Ind. Eng. Chem.*, 1933, 25, 973.

The flexible alkyd resins can be cast into sheets or rods and then cured at 125°C. or over. The harder-cured resins (i.e., containing a high proportion of glycerol phthalate) may be milled, machined or pressure molded. They may be obtained

<sup>44</sup> H. Schuchmann and F. Streuber, German P. 553,005, 1928, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1932, 26, 4718. Allgemeine Elektrizitäts-Ges., British P. 303,867, 1929, to International General Electric Co.; *Brit. Chem. Abs. B*, 1930, 456. See Chapter 47.

<sup>45</sup> W. H. Carothers and J. W. Hill, *loc. cit.*

<sup>46</sup> R. H. Kienle and P. F. Schlingman, *Ind. Eng. Chem.*, 1933, 25, 971. See J. G. E. Wright, *Trans. Am. Inst. Chem. Eng.*, 1932, 28, 21.

in a transparent state and offer a non-inflammable substitute for celluloid. The very flexible resins display a remarkable sound-absorbency and facility for dampening vibrations. Such resins have found application further as lacquer plasticizers, as a base for heat- and oil-resistant varnish cloths and as gaskets.

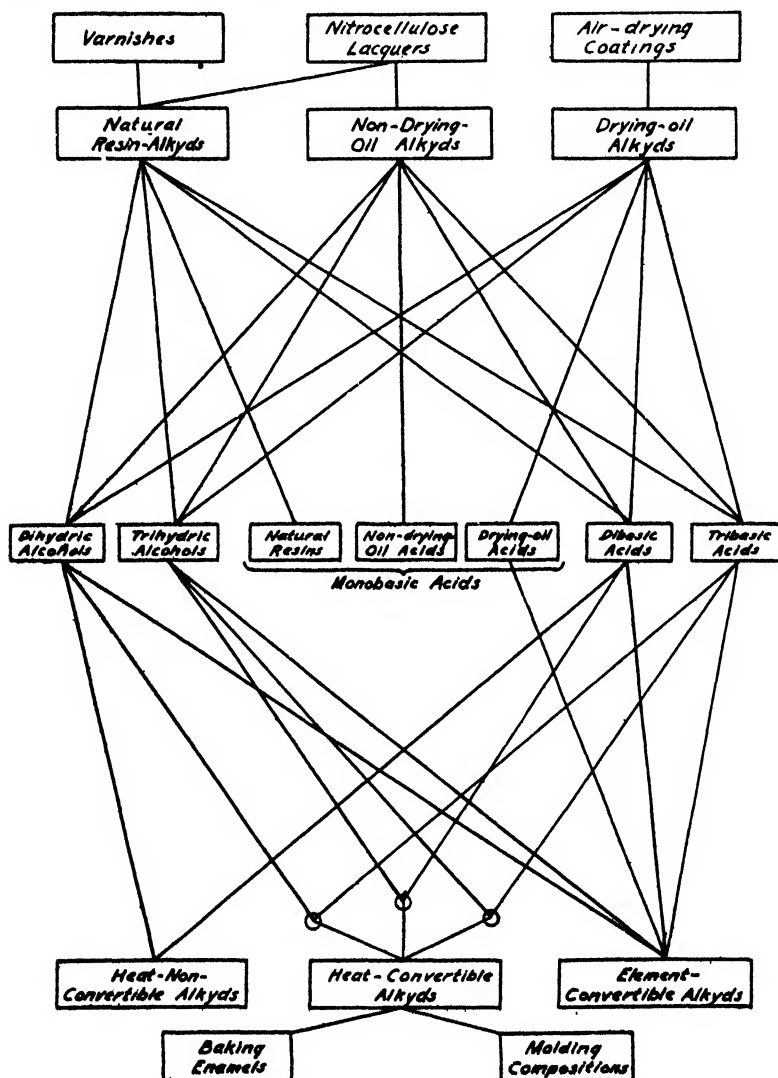


FIG. 125.—Relationships Among Alkyd Resins.

**Monobasic Acid-Modified Resins.** Addition of monobasic acids to the alkyd type of resin modifies the properties considerably. The alkyd resins, according to the type of monobasic acid may be non-drying, semi-drying or drying. The non-drying type of alkyd resin is used mostly in nitrocellulose lacquers as a resin or plasticizer or both. Castor oil also finds use in these nitrocellulose lacquer

alkyds. The semi-drying-oil alkyds can be baked at high temperatures and show no tendency to wrinkle under this treatment. The short-drying alkyds may be baked rapidly and exhibit unusual hardness and good adhesion.<sup>47</sup> They can also be air-dried.

By the interaction of linseed oil fatty acids (1 equivalent) and phthalic anhydride (2 equivalents) on glycerol (3 equivalents), a product is obtained simulating bodied linseed oil. It displays on heating both the element-convertibility of the drying oils and the heat-convertibility of the alkyd resins, according to Hönel.<sup>48</sup>

**Alkyd Resin Modifications.** Due to various modifications, alkyd resins have been classified in several ways. Krumbhaar<sup>49</sup> suggests the following groups: (1) Straight alkyds, (2) phenol-modified alkyds, (3) phenol-modified and oil-extended and (4) non-phenolic, modified by natural resin acids. Malowan<sup>50</sup> uses the classification: (1) Unsaturated modifications containing fatty acid residues and compatible with nitrocellulose lacquers, (2) modified with natural resin acids, (3) unsaturated containing drying oils and (4) mixed types from natural and synthetic resins.

The divisions which will be adopted in this instance depend upon the use of: (1) non-drying oils and acids, (2) natural resins, (3) various drying oils and acids and (4) other synthetic resins. In Figure 125 are shown the inter-relationships and ramifications of the alkyd resins. The very center of the diagram reveals the various ingredients used in making up the resins. From the ingredients it is possible to trace the various types which may be synthesized. Thus the heat-non-convertible resins are prepared from dihydric alcohols and dibasic acids. Heat-convertible alkyds may be made from dihydric alcohols and tribasic acids, from dihydric alcohols and tribasic acids or from tribasic acids and trihydric alcohols. It will be noted that the element-convertible alkyds correspond to the drying-oil alkyds. Use of such acids as non-drying or natural resin acids yields other derivatives which do not correspond to the convertible and non-convertible types.

<sup>47</sup> W. Krumbhaar, *Paint, Oil, Chem. Rev.*, 1934, 96 (12), 7, 8, 29; *Chem. Abs.*, 1934, 28, 4920.

<sup>48</sup> H. Hönel, *ibid.*, 1931, 91 (35), 25; *Chem. Abs.*, 1931, 25, 3854. The chemical reactions that take place in stand-oil are not too well understood but according to C. A. P. Kappelmeier (*Chem. Weekblad*, 1934, 31, 423) higher acids may be formed and these can be formulated on the basis of the diene synthesis. (See Chapter 40.) E. Fonrobert and F. Pallaut (*Chem. Umschau Fette, Oele, Wachse, Harze*, 1926, 33, 41; *Chem. Abs.*, 1926, 20, 2418) and W. E. Wornum (*J. Oil, Colour Chem. Assoc.*, 1933, 16, 231; *Chem. Abs.*, 1933, 27, 4694) have called attention to the similarities which may exist between tung oil and the alkyd resins. For the temperature coefficients and energy of activation of the heat-convertible, heat-non-convertible and element-convertible resins, see R. H. Kienle, *Ind. Eng. Chem.*, 1930, 22, 590.

<sup>49</sup> W. Krumbhaar, *loc. cit.* These divisions are based on the solubilities of the alkyd resins determined by adding methylated spirit, ethyl acetate and white (mineral) spirit to toluene solutions. See *Paint, Oil, Chem. Rev.*, 1934, 96, 18.

<sup>50</sup> S. Malowan, *Synthetic and Applied Finishes*, 1934, 5, 85.

## Chapter 42

### Alkyd Resins. Production

The reaction products of polyhydric alcohols and polybasic acids form a very important group of resinous substances. Glycol, glycerol and their homologues are typical polyhydric alcohols. The more common polybasic acids include phthalic, tartaric, citric, succinic, maleic and malic, and in addition there are many other acids of this type which are less easily available.

Phthalic glyceride, the reaction product of glycerol and phthalic anhydride, serves as a basis of comparison for the resins of this group. This chapter includes the investigations relating to this resin and others which may be formed from polybasic acids and polyhydric alcohols, that is, two-component resins. When part of the polybasic acid or polyhydric alcohol is replaced by other types of acid or alcohol, or when any other ingredient enters into the composition, more complex resins having different properties are obtained.

In 1901, in an attempt to make a phthalein dye, Watson Smith<sup>1</sup> heated for a long time nearly to boiling a mixture of 2 mols glycerol and 3 mols phthalic anhydride (the proportions corresponding to diglyceryl triphthalate) and on cooling, a solid resin-like, perfectly transparent and strongly refractive substance was obtained. This substance was insoluble in water, but soluble in an excess of glycerol on heating. From the solution in glycerol the addition of water caused the separation of white oily drops soluble in alcohol and ether. Similar resin-like masses were made using zinc chloride; these deliquesced and became sticky on exposure to air. Upon distilling *in vacuo* to remove the excess of glycerol a mass resembling glass slag was obtained; the end point of the distillation was noted when frothing set in. The same compound was obtained regardless of whether an excess of either phthalic anhydride or of glycerol was used. The resin was easily saponified by alkali hydrates. Smith varied the fusibility of the resin by stopping the vacuum distillation of the glycerol at some intermediate point. The initial melting point (190°C.) and the decomposition point (220°C.) were not far apart. At the latter temperature the resin did not completely melt and crystals of phthalic anhydride distilled off which were deposited on the sides of the tube. The resin ignited readily and burned with a bright flame but softened without melting. Smith recommended it as a cement for glass and earthenware.

The next investigator of phthalic glyceride was Callahan.<sup>2</sup> He gave certain details of operation as follows: One part by weight of glycerol and 2 parts of phthalic anhydride are heated slowly. At 100°C. the mixture forms a clear liquid and as the heating continues, distillation occurs to a slight extent. At 185°C. the temperature rise should be checked until distillation ceases. Then the heating is continued at a higher temperature, about 210°C., until the first stage of the reaction is completed. This point is ascertained by withdrawing small samples, cooling and observing if these are hard and brittle without stickiness. The resin is yellowish and transparent. If the heating is continued at 210°C., further change

<sup>1</sup> W. Smith, *J.S.C.I.*, 1901, 20, 1075.

<sup>2</sup> M. J. Callahan, *U. S. P.* 1,108,329, Aug. 25, 1914; *Chem. Abs.*, 1914, 8, 3506.

takes place with the evolution of heat. At 275°C. a violent ebullition sets in and there results a brittle infusible mass filled with cavities. Even at 210°C. some vesiculation occurs.

Callahan<sup>a</sup> prevented vesiculation when carrying out the transformation or polymerization to an insoluble product by heating at 85-100°C. (or even 135°C.) for a considerable period, say 15 to 20 hours. The product is a homogeneous dense resin which softens at temperatures above 40°C. but never actually melts without decomposition. It may be molded with a filler in various ways. The insoluble product possesses high dielectric strength and good insulating properties. Alkali saponifies the resin to regenerate glycerol and the corresponding phthalate. Callahan also proposed to employ glycol and carbohydrates (glucose, sucrose, starch, and cellulose) instead of glycerol.

The resin described above does not represent the final product. Callahan found this resin to be affected by water. On standing for several weeks in contact with water the surface of the insoluble resin became white and cheesy. Long exposure to the weather caused it to become white and crumbly. Callahan termed this product an intermediate resin and made further experiments on the effect of heat treatment leading to a final form having notable resistance to water. The procedure he recommended is to heat the intermediate product for 5-10 hours at 180-250°C. At this temperature condensation is completed and any traces of free glycerol are eliminated. The resin is insoluble in all the usual solvents but like the intermediate product is soluble in glycerol. The final product is not attacked in the cold by alkaline solutions. At 140°C. the resin becomes leathery and may be bent or molded.

The water formed during esterification distills off as fast as it is formed, especially if the heating is carried out in an open vessel, or (as is usually the case) under a short air-condenser. It may also be eliminated by the addition of an inert, water-insoluble organic liquid capable of forming a pseudo-azeotropic mixture with water. Xylene, cyclohexane or acetylene tetrachloride may be used.<sup>4</sup> The reaction can also be carried out in the presence of high-boiling inert liquids like tetralin or dekalin which are later distilled off along with the water of reaction.<sup>5</sup>

The resin produced from glycerol and phthalic anhydride is practically colorless when the condensation is carried out in an atmosphere of carbon dioxide or of hydrogen, or in a vacuum.<sup>6</sup> Another method of treating the resin is to spray the aqueous mixture into an inert atmosphere.<sup>7</sup>

#### STAGES OF RESINIFICATION

According to Weisberg<sup>a</sup> the condensation of glycerol with polybasic acids takes place in three stages.

A. The initial condensation product is soluble in acetone and is fusible. Its melting point seldom exceeds 120°C. This resin is not resistant to cold water but on further heating passes over into a resin of class B.

B. This resin is an intermediate condensation product, practically insoluble in acetone and difficultly fusible, although it can be molded under heat and pressure. Like the resins of class A it is not resistant to cold water. On heat treatment it is converted into a resin of class C.

<sup>a</sup> M. J. Callahan, U. S. P. 1,108,330, Aug. 25, 1914; *Chem. Abs.*, 1914, 8, 3506.

<sup>4</sup> British P. 352,981, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5440. French P. 704,657, 1930; *Chem. Abs.*, 1931, 25, 4553.

<sup>5</sup> British P. 363,029, 1930, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1933, 27, 1531.

<sup>6</sup> British P. 296,787, 1927, to International Gen. Elec. Co.; *Chem. Abs.*, 1929, 23, 2585.

<sup>7</sup> British P. 408,689, 1934, to Bakelite Corp.; *Chem. Abs.*, 1934, 28, 5093.

<sup>a</sup> L. Weisberg, U. S. P. 1,413,144 and 1,413,145, Apr. 18, 1922, to Barrett Co.; *J.S.C.I.*, 1922, 42, 667A. British P. 173, 225, 1921; *J.S.C.I.*, 1923, 42, 667A.

C. This resin represents the final condensation product. It is insoluble in acetone and infusible, but it can be molded under heat and pressure. It is resistant, moreover, to both cold and boiling water. The resin produced from glycerol and phthalic acid is very brittle and the addition of an aliphatic acid tends to reduce brittleness, although probably diminishing resistance to water. In fact, a tougher and more elastic product is obtained when a substantial proportion of a dibasic aliphatic acid (succinic, malic, tartaric, maleic or fumaric acid) is present.

The C-stage products are superior to B-stage resins in hardness and resistance to water and solvents. They are intractable substances, however, and require drastic treatment to make them useful unless they are formed under such conditions that they can be used directly as produced, as for example, in molded articles or baked coatings.

The B-stage resins swell rather rapidly and become gelatinous in hot acetone. Weisberg<sup>22</sup> used glycerol phthalate in the B-stage. The resin is treated with hot acetone and mixed with fillers. The acetone is then distilled off and the product molded. Curing time is shorter than that of a molding composition made from resin in the A-stage. Wright<sup>9</sup> also used the B-stage with swelling agents along with a plasticizer. This plasticizer may be added directly or the resin may have its own plasticizer in the form of an ester from the ingredients used. One may also dissolve the A-resin in a B-resin solvent (e.g., cyclohexanol) and heat the solution to convert the resin into the B-state; the filler being introduced at any convenient stage before pressing.<sup>10</sup>

It is possible to prepare colorless resinous bodies, which are hard, tough and infusible, from the initial reaction products of phthalic anhydride and glycerol by sufficiently prolonged baking of the resin at a moderate temperature. The time necessary to achieve this result is, as compared with most chemical reactions, very long, but varies with the size of the piece or block, with the temperature and with the degree of hardness desired. For molded blocks or slabs of moderate size a heat-treatment of several weeks or even months may be necessary. For example, blocks approximately  $4 \times 4 \times \frac{1}{4}$  inches require heating at about 125°C. for a period of 12 weeks.

Schmidt<sup>11</sup> heated a mixture of one part by weight of glycerol with 2 parts of phthalic anhydride to about 150° to 175°C. until the first condensation was complete. The resulting condensation product was poured into molds, and maintained at about 90°C. until it assumed a firm, rubbery consistence. The temperature was then gradually increased to about 125°C. and maintained until the resin became infusible. The product is transparent, free from bubbles or flaws, practically colorless, tough, infusible, and sufficiently thermoplastic to allow it to be molded under heat and pressure. The final hardening may also be carried out in a mold under pressure at a temperature of about 170°C. It is advisable to use molds made of aluminum or stainless steel or to line the molds with aluminum or vitreous enamel.<sup>12</sup> Another resin of the glycerol phthalate type which is insoluble in water, neutral and soluble in organic solvents is obtained by carrying out the reaction at a low temperature and by separating the neutral glycerol phthalate formed during the reaction. The reaction mass is taken up in an organic solvent

<sup>22</sup> L. Weisberg, U. S. P. 1,443,936, Jan. 30, 1923, to Barrett Co.; *Chem. Abs.*, 1923, 17, 1842.

<sup>9</sup> J. G. E. Wright, British P. 294,450, 1933 to British Thomson-Houston Co.; *Chem. Abs.*, 1934, 24, 323.

<sup>10</sup> British P. 360,571, 1930, to Bakelite G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 356.

<sup>11</sup> J. H. Schmidt, U. S. P. 1,663,183, Mar. 30, 1928, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 1696. British P. 306,068, 1927; *Chem. Abs.*, 1929, 23, 4090. French P. 633,064, 1927; *Chem. Abs.*, 1929, 23, 293. Canadian P. 300,792, 1930. Belgian P. 343,436, 1927. Italian P. 290,483, 1928.

<sup>12</sup> H. W. H. Warren, R. Newbould and A. T. Ward, British P. 252,646, 1927, to British Thomson-Houston, Co., Ltd.; *Chem. Abs.*, 1929, 23, 1517. French P. 642,657, 1928, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 3115. German P. 330,707, 1928, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1929, 26, 394.

(acetone or alcohol) which dissolves the neutral phthalates; addition of alkali precipitates the resin.<sup>13</sup>

#### ACCELERATION OF CONVERSION

Resins may be converted to the infusible-insoluble, or C-stage, without the formation of a frothy mass if the intermediate form is heated under pressure, or at a moderate temperature without pressure, but these operations are usually unsatisfactory on account of the length of time required. It is important commercially to shorten the curing time as much as possible.

If the initial resin is heated at 205°C. to a stage just short of its conversion to the insoluble C-stage, the period of baking is reduced. As soon as a sample of resin, cooled to about 180°C. shows signs of stringing, the entire mass is poured out into shallow pans to cool it rapidly, and the resin is afterward baked at a moderate temperature until it becomes infusible.<sup>14</sup>

Another way of controlling the conversion to the infusible stage is to heat the initial resin until a sample is hard and brittle when cold. The entire mass is then allowed to cool and is pulverized. This finely divided resin is heated in a rotating oven at 100°C., the temperature is gradually increased as the resin gets harder, and finally it is heated for about 4 hours at 225°C., the treatment being stopped before the particles reach the stage of complete infusibility. The powder thus obtained may be used directly for molding.<sup>15</sup>

Wright and Bartlett<sup>16</sup> dissolved the initial resin in an inert, high-boiling solvent (diethyl phthalate or benzyl benzoate) and heated the solution until the resin was almost converted to the insoluble stage. A solution of the resin in diethyl phthalate (b.p. 295°C.) is heated to between 210-290°C. without a reflux condenser (to eliminate volatile materials) until the resin is just short of the insoluble stage. After heating, the solution is poured into benzene which precipitates the resin as a white curd, which is dried and ground to a powder. The product is slowly soluble in acetone and unlike ordinary glycerol phthalate is non-corrosive to metals. It is converted to the final hard form in a shorter time than a resin which has not been treated in this way.

A similar procedure was used by Schmidt.<sup>17</sup> In this instance the phthalic anhydride and glycerol were dissolved in diethyl oxalate or glycol diacetate and the solution was heated to the stage of incipient gelatinization of the resin. A medium-boiling solvent is then added to form a solution of highly polymerized resin.

Adams<sup>18</sup> allowed the resin to reach the infusible vesiculated condition by heating it to about 300°C. and ground the mass after cooling. Although the resin in this condition is insoluble in all organic solvents in the cold, it may be dissolved by protracted heating at a high temperature under pressure in a large number of organic liquids which are solvents for both glycerol and phthalic anhydride, among which may be mentioned glycol diacetate, diethyl phthalate, acetone, acetone oils, benzyl

<sup>13</sup> French P. 752,620, 1933, to Soc. française Duco; *Chem. Abs.*, 1934, 28, 1203.

<sup>14</sup> J. H. Schmidt, U. S. P. 1,739,771, Dec. 17, 1929, to Bakelite Corp.; *Chem. Abs.*, 1930, 24, 961. French P. 638,253, 1929; *Chem. Abs.*, 1930, 24, 4648. British P. 336,645, 1929; *Brit. Chem. Abs. B*, 1930, 1164.

<sup>15</sup> W. R. May, U. S. P. 1,853,178, Apr. 5, 1932, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1932, 26, 3125. German P. 572,135, 1923, to Siemens-Schuckertwerke A.-G.; *Chem. Abs.*, 1933, 27, 3096.

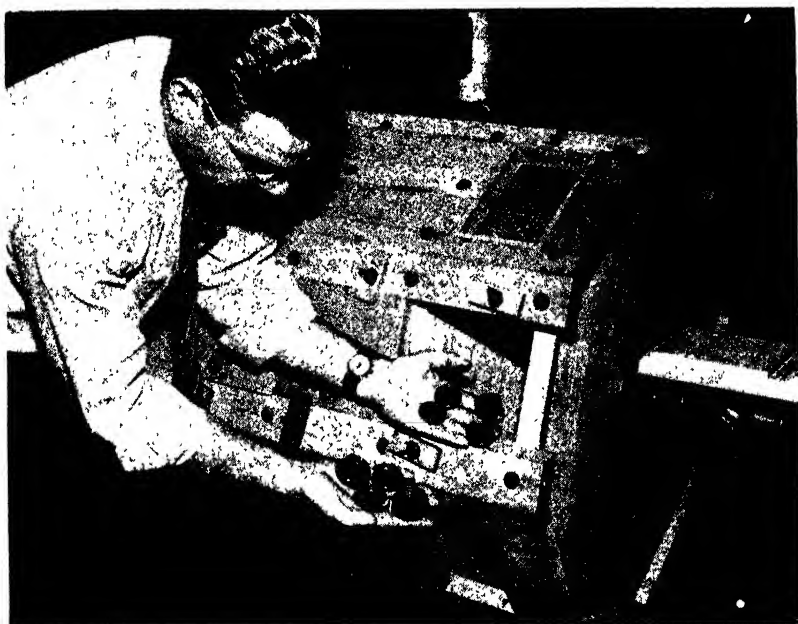
<sup>16</sup> J. G. E. Wright and W. J. Bartlett, U. S. P. 1,634,969, July 5, 1927, to General Electric Co.; *Chem. Abs.*, 1927, 21, 2993. British P. 235,589, 1924, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1926, 20, 997. Canadian P. 262,399, 1923, to Canadian General Electric Co.; *Chem. Abs.*, 1926, 20, 3580. German P. 448,652, 1927, to Allgemeine Elektrizitäts-Ges.

<sup>17</sup> J. H. Schmidt, British P. 275,604, 1927, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1929, 294. French P. 638,121, 1927; *Chem. Abs.*, 1929, 23, 293. German P. 552,065, 1933; *Chem. Abs.*, 1934, 28, 1832. Belgian P. 343,427, 1927. Italian P. 260,454, 1923.

<sup>18</sup> L. V. Adams, U. S. P. 1,849,817, Mar. 15, 1932, to General Electric Co.; *Chem. Abs.*, 1932, 26, 2690. British P. 273,748, 1926, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1928, 22, 2072. French P. 23,789, 1927, addn. to 804,198, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 3589. Canadian P. 289,812, 1929, to Canadian General Electric Co., Ltd.

benzoate, benzyl acetate, toluidine, benzyl alcohol, cresol, tricresyl phosphate, triacetin, anisol, o-cresyl benzoate, ethyl lactate, indene and indene polymer. Heating in a closed container for about 36 hours at 170°C. is necessary for solution.

The temperature of hardening soluble resins made from polyhydric alcohols and polybasic acids is reduced by treatment with an acid (sulphurous, hydrochloric, hydrofluoric, formic or acetic acids) of stronger acidity than the acid component of the resins.<sup>19</sup>



*Courtesy Modern Plastics*

FIG. 126.—Buttons Before and After Tumbling Operation.

The time required to convert the resin to the intusible state may also be reduced by treating the initial resin with an acid anhydride or an acid chloride. The excess is removed by heating the resin at ordinary or reduced pressure. For example, 100 parts by weight of fusible glycerol-phthalate resin are treated with 10 parts of acetic anhydride at 120°-130°C. for about an hour. Heating the resulting product at 125°-130°C. in a vacuum removes the excess reagent and yields a resin which cures more rapidly than an untreated one.<sup>20</sup>

Arsem<sup>21</sup> found that sulphonic acids have an accelerating effect both in the

<sup>19</sup> British P. 317,225, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1997. French P. 672,177, 1929; *Chem. Abs.*, 1930, 24, 2317.

<sup>20</sup> H. W. Warren, R. Newbound and A. T. Ward, U. S. P. 1,902,477, Mar. 21, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 3351. French P. 39,430, 1930, addn. to 661,518, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 2334. British P. 346,333, 1929, to British Thomson-Houston Co.; *Chem. Abs.*, 1932, 26, 2072. German P. 564,956, 1930, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1933, 27, 1231.

<sup>21</sup> W. C. Arsem, U. S. P. 1,560,164, May 24, 1932, to General Electric Co.; *Chem. Abs.*, 1932, 26, 3945. French P. 696,795, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 3503. British P. 353,249, 1930, to British Thomson-Houston Co.; *Brit. Chem. Abs. B.* 1931, 1107. Canadian P. 322,366, 1932, to Canadian Gen. Elec. Co., Ltd.; *Chem. Abs.*, 1932, 26, 3687. German P. 580,931, 1932, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 1208.



formation of the initial resin and in the conversion of this product to the infusible state. When 1 to 5 per cent of such acids as benzene sulphonic, 1-naphthylamine-4-sulphonic or 4-aminotoluene-2-sulphonic acids is used, the time required to form the initial resin from phthalic anhydride and glycerol may be reduced to only one-sixth of the period necessary and the initial resin hardens in a relatively short time. Neutral phenyl benzenesulphonate and other sulphonic acid esters have been used by Carswell.<sup>22</sup>

The addition of zinc oxide or calcium oxide lowers the solidification temperature.<sup>23</sup> Wright<sup>24</sup> recommended heating the resins with dehydration catalysts (calcium oxide, magnesium oxide, zinc oxide or finely divided iron or zinc) to convert them to the insoluble form. Metallic soaps, incorporated with the resin during its formation, yield a tougher and more shock-resistant product which sets more quickly under heat treatment. Adams<sup>25</sup> heated a mixture containing 68.8 parts of phthalic anhydride, 28.3 parts of glycerol and 2.9 parts of cobalt linoleate to form a similar resin. Lead oleate, aluminum stearate and metallic linoleates are other soaps and salts which act in the same way.

Rosenstein and Hund<sup>26</sup> used silica gel<sup>27</sup> as an esterification catalyst in the reaction between glycerol and phthalic anhydride; Ushakov<sup>28</sup> employed mineral salts, metallic oxides or metals, with or without pressure.

Blumer<sup>29</sup> reduced the acidity of the resin and removed uncombined initial materials both in one step by treating the resin in an intermediate stage of condensation through use of ethyl, methyl, butyl or propyl alcohols. For example, the condensation product derived from glycerol, phthalic acid and citric acid is dissolved in a small amount of alcohol or in alcoholic benzene; the solution is separated into two layers by the addition of ethyl alcohol. The residual resin has a much improved heat-hardening rate.

#### RETARDATION OF CONVERSION

If fillers are to be impregnated with the molten resin a difficulty arises, in that hardening takes place rendering impregnation difficult. Callahan<sup>30</sup> avoided the hardening by adding naphthalene (preferably 13-18 per cent) to the resin. Monochloro- and tetrachloronaphthalene or anthracene can also be used. These substances allow the resin to liquefy at a lower temperature than that necessary for the straight resins, and consequently gelation occurs less quickly. The addition of from 1-10 per cent of boric acid is said to retard the formation of insoluble masses.<sup>31</sup> Urea or thiourea added to the polyhydric alcohol and polybasic acid resin causes the resin to gel or polymerize more slowly.<sup>32</sup>

<sup>22</sup> T. S. Carswell, U. S. P. 1,924,396, Aug. 29, 1933, to Monsanto Chemical Co.; *Chem. Abs.*, 1933, 27, 5561.

<sup>23</sup> Carleton Ellis, U. S. P. 1,897,977, Feb. 14, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 2632.

<sup>24</sup> J. G. E. Wright, U. S. P. 1,581,902, Apr. 20, 1926, to General Electric Co.; *Chem. Abs.*, 1926, 20, 1918. British P. 236,591, 1925, to British Thomson-Houston Co., Ltd.; *J.S.C.I.*, 1925, 770B. German P. 555,534, 1925, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1925, 26, 6167.

<sup>25</sup> L. V. Adams, U. S. P. 1,805,473, May 19, 1931, to General Electric Co.; *Chem. Abs.*, 1931, 25, 3856. British P. 310,854, 1928, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1930, 24, 740. French P. 26,837, 1929, addn. to 616,463, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 1110. Canadian P. 321,619, 1932, to Canadian Gen. Elec. Co., Ltd.; *Chem. Abs.*, 1932, 26, 3292. German P. 537,364, 1929, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1932, 26, 1144.

<sup>26</sup> L. Rosenstein and W. J. Hund, U. S. P. 1,851,405, March 29, 1932; *Chem. Abs.*, 1932, 26, 2068.

<sup>27</sup> On the use of silica gel in other esterifications see A. Korolev, *J. Chem. Ind. (Moscow)*, 1937, 4, 547; *Chem. Abs.*, 1938, 22, 944.

<sup>28</sup> S. N. Ushakov, Russian P. 32,157, 1933; *Chem. Abs.*, 1934, 28, 3606.

<sup>29</sup> L. Blumer, British P. 406,444, 1934, to Firma Louis Blumer; *Chem. Abs.*, 1934, 28, 4924. French P. 748,720, 1933; *Chem. Abs.*, 1933, 27, 5339. See German P. 546,605, 1936; *Chem. Abs.*, 1932, 26, 3644.

<sup>30</sup> M. J. Callahan, U. S. P. 1,108,331, Aug. 25, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 3506.

<sup>31</sup> British P. 353,491, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 1147. French P. 714,372, 1931; *Chem. Abs.*, 1932, 26, 1813.

<sup>32</sup> T. F. Bradley, British P. 412,172, 1934, to American Cyanamid Co.; *Chem. Abs.*, 1934, 28, 7864.

## IMPROVING FLEXIBILITY

Various plasticizers (soft resins or liquids) may be mixed with phthalic glyceride to improve its flexibility. Callahan<sup>33</sup> and Arsem<sup>34</sup> used succinic glyceride which was formed *in situ*. Dawson<sup>35</sup> found m-dinitrobenzene, acetanilide and ethyl benzoate to be useful with citric glyceride.

The disadvantage of using the glycerides of aliphatic dibasic acids (succinic) to increase the flexibility of phthalic glyceride is that the effect is not permanent. When heated for a long time or when aged the mixed resin becomes brittle and tends to have a high acid number. Glycols give highly esterified bodies which remain soft for an indefinite period but they retain solubility at all times and do not cure. Kienle and Rohlf<sup>36</sup> have suggested the incorporation of glycol succinate with phthalic glyceride in such amounts that the composition cures when heated at a high temperature. About one mol of each resin may be used. The resins may be prepared separately and then mixed, or all ingredients may be heated together at 180-200°C. Curing is carried out at 150°C. and a soft, flexible product is obtained.

High-boiling solvents were used to increase flexibility by Conover,<sup>37</sup> who mixed 15 parts of diethyl phthalate with 85 parts of freshly prepared phthalic glyceride and heated the solution to 150°C. A soft, light-colored resin was obtained which could be converted into a flexible, infusible form by heating to a high temperature. Kienle<sup>38</sup> added dibutyl phthalate, triphenyl phosphate, triacetin or aniline to overcome the brittleness of phthalic glyceride.<sup>39</sup> The addition of furfural increases flexibility but also has a tendency to darken the color. Conover<sup>37</sup> heated a mixture containing 92 parts of glycerol and 148 parts of phthalic anhydride at 210°C. for an hour, allowed the temperature to fall to 140°C. and added 48 parts of furfural, producing a soft, dark-colored mass. This product is converted to the infusible form when heated, the conversion being about 10 times as rapid as that of the resin in the absence of furfural.

Amino-carboxylic acids may be added at any stage before the conversion of the resin to its final form. The amino acid may be formed *in situ* as for example by the action of chloroacetic acid on aniline. Blue-colored resins of improved mechanical and electrical properties are formed.<sup>40</sup>

Harder and more water-resistant glycerol phthalate resins are prepared by treatment with ketene. The free hydroxyl groups in the glycerol phthalate resin are acetylated under these conditions.<sup>41</sup> Glycerol, 29.7 parts, is heated with 70.3 parts of phthalic anhydride for 4 hours at 200°C. until the resin has an acid value

<sup>33</sup> M. J. Callahan, U. S. P. 1,108,332, Aug. 25, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 3506.

<sup>34</sup> W. C. Arsem, U. S. P. 1,088,776, June 2, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 2816. *British P.* 24,254, 1912, to General Electric Co.; *Chem. Abs.*, 1914, 8, 1243.

<sup>35</sup> E. S. Dawson, Jr., U. S. P. 1,085,112, Jan. 27, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 1215.

<sup>36</sup> R. H. Kienle and H. C. Rohlf, U. S. P. 1,897,360, Feb. 14, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 2831. *British P.* 385,140, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 1775. *French P.* 701, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 4139.

<sup>37</sup> C. Conover, U. S. P. 1,693,082, July 13, 1926, to Selden Co.; *Chem. Abs.*, 1926, 20, 3242. *British P.* 231,742, 1926, to Selden Co.; *Chem. Abs.*, 1928, 22, 3792.

<sup>38</sup> R. Kienle, *British P.* 275,219, 1926; *Chem. Abs.*, 1928, 22, 2282. See also V. H. Turkington, U. S. P. 1,695,696, Dec. 15, 1928, to Bakelite Corp.; *Brit. Chem. Abs. B.*, 1929, 444.

<sup>39</sup> Diphenyl phthalate has also been suggested as a flexibilizing agent. See T. S. Carswell, U. S. P. 2,006,245, July 2, 1935, to Monsanto Chemical Co.

<sup>40</sup> C. Conover, U. S. P. 1,678,105, July 24, 1928, to Selden Corp.; *Chem. Abs.*, 1928, 22, 3543.

<sup>41</sup> German P. 533,164, 1933, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 363. The neutral product may in turn be further polymerized by heating. See German P. 533,924, 1934, to Degussa A.-G. (Anorgewerkstoff); *Chem. Abs.*, 1934, 28, 3607.

<sup>42</sup> For the treatment of glycerol phthalate resins with monobasic acids see Chapters 43 and 44.

of 120-130. Ketene ( $\text{CH}_2=\text{C}=\text{O}$ ) is then passed through a 50 per cent acetone solution of the resin, the temperature being maintained at  $50^\circ\text{C}$ . until the exothermic reaction is complete. The product thus formed is darker in color and has a higher acid number than the original resin but is more resistant to water. The ketene-treated resin is compatible with nitrocellulose.<sup>42</sup>

A great many other modifying agents may be combined in the resin molecule for the same purpose or to produce resins of different properties. Such chemically modified resins are the subject of the chapters immediately following.

#### OTHER POLYBASIC ACIDS

Of the aromatic polybasic acids, other than phthalic,<sup>43</sup> Downs and Weisberg<sup>44</sup> suggested diphenic and 1,8-naphthalic acids. These aromatic acids are not as easily available as phthalic (see Fig. 126) and, when an acid other than phthalic is to be used, it may be selected from the aliphatic polybasic acids (succinic, maleic, fumaric, malic, malomalic, citric, aconitic, adipic, azelaic, sebacic, diglycolic and thiodiglycolic acids).<sup>45</sup>

TABLE 43.—Polybasic Acids.

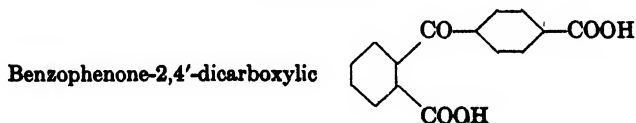
##### Aliphatic Acids

Carbonic	$\text{HO}-\text{COOH}$
Oxalic	$\text{HOOC}-\text{COOH}$
Succinic	$\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$
Malic	$\text{HOOC}-\text{CHOH}-\text{CH}_2-\text{COOH}$
Tartaric	$\text{HOOC}-\text{CHOH}-\text{CHOH}-\text{COOH}$
Maleic	$\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$ (cis)
Fumaric	$\text{HOOC}-\text{CH}=\text{CH}-\text{COOH}$ (trans)
Citric	$\text{HOOC}-\text{CH}_2-\text{C}(\text{OH})(\text{COOH})-\text{CH}_2-\text{COOH}$
Glutaric	$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
Adipic	$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
Pimelic	$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
Suberic	$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
Azelaic	$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$
Sebacic	$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{COOH}$

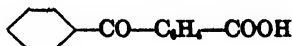
##### Ether Acids

Diglycolic	$\text{HOOC}-\text{CH}_2-\text{O}-\text{CH}_2-\text{COOH}$
Dilactic	$\text{HOOC}-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}(\text{CH}_3)-\text{COOH}$
Dihydracrylic	$\text{HOOC}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{COOH}$
Salicylactic	$\text{HOOC}-\text{C}_6\text{H}_4-\text{O}-\text{CH}_2-\text{COOH}$

##### Ketone Acids



Benzoylbenzoic (monobasic)



<sup>42</sup> M. M. Brubaker and G. D. Graves, U. S. P. 1,908,828, Mar. 12, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 8071; British P. 419,573, 1933; *Brit. Chem. Abs.* B, 1935, 112.

<sup>43</sup> A. O. Jaeger (U. S. P. 1,959,987, Apr. 10, 1934, to Selden Research & Eng. Corp.; *Brit. Chem. Abs.* B, 1935, 140) purified the phthalic anhydride, obtained by the aerial oxidation of anthracene, by refluxing or distilling over polymerization catalysts such as pumice, zeolites, silicas, alumina and zinc oxide.

<sup>44</sup> C. R. Downs and L. Weisberg, U. S. P. 1,488,744, Apr. 8, 1924, to Barrett Co.; *Chem. Abs.*, 1924, 18, 1917; British P. 173,335, 1931, to Barrett Co.; *J.S.C.I.*, 1933, 42, 667A.

<sup>45</sup> P. Pfeiffer and R. Hansen (*J. prakt. Chem.*, 1931, 130, 1; *Chem. Abs.*, 1931, 25, 3544) have discussed the determination of the equivalent weight of organic acids in the crystalline state by passing dry ammonia over the dry acid to constant weight.

TABLE 43.—Polybasic Acids (Continued)

*Cyclic Dibasic Acids*

Phthalic acid	
Diphenic acid	
1,8-Naphthalic acid	
Camphoric	
Tetrahydrophthalic acid	
3,6-Endomethylene-Δ <sup>4</sup> -tetrahydrophthalic acid	

Halogenated acids (tetrachlorophthalic anhydride,<sup>46</sup> chlorosuccinic, chloromalic and halogenated fumaric and sebacic acids)<sup>47</sup> have also been recommended. Other types are aromatic ketone-acids and the condensation products obtained when maleic anhydride reacts with either vinyl acetate or styrene. Examples of simple polyhydric alcohol resins, made from these acids, will now be described.

<sup>46</sup> G. Walter, *Monatsh.*, 1934, 64, 287; *Chem. Abs.*, 1935, 29, 153. The tetrachlorophthalic acid was prepared by the action of chlorosulphonic acid on naphthalene.

<sup>47</sup> F. Zwillgmeier, U. S. P. 1,950,468, Mar. 13, 1934, to National Aniline & Chem. Co.; *Chem. Abs.*, 1934, 28, 3255.

<sup>56</sup> Certain of the carbonic esters find a use. The  $\beta,\beta$ -dialkoxyethyl carbonates, either the methoxy or the ethoxy, may be employed as plasticizers for cellulose acetate. See H. B. Smith, U. S. P. 1,905,518.

**Succinic Acid.**  $(\text{HOOC}-(\text{CH}_2)_2-\text{COOH})$ .<sup>17</sup> A product called succinin was obtained by van Bemmelen<sup>18</sup> on heating equal weights of succinic acid and glycerol to 130°C. More glycerol was thus present than corresponded to the acid equivalent. The product was a thick syrup and when heated to 200-220°C. for several hours the mass became hard and tough, losing all acid taste. The resinous material was of a brownish black color, insoluble in water, alcohol, ether or carbon disulphide. When boiled with alcohol and water it slowly decomposed, forming a syrupy substance. The resin likewise dissolved on treatment with caustic alkali solutions or with a suspension of lead oxide. On heating one equivalent each of succinic and benzoic acids and somewhat more than one equivalent of glycerol, water was driven off at about 100° and at 140°C. benzoic acid began to sublime. Additional quantities of benzoic acid were added and the mixture was heated to 200°C. for several hours until sublimation no longer took place. When hot the product was a viscous black mass, cooling to a tough elastic substance which could be drawn into threads. It was insoluble in alcohol, ether and water but decomposed slowly on boiling with water. It dissolved readily in hot alkaline solutions. Van Bemmelen observed that succinic acid combined quickly with the glycerol whereas benzoic acid combined later and with less readiness. The product was called benzosuccinin. Funaro and Danesi<sup>19</sup> also prepared succinin according to van Bemmelen's method by heating succinic acid and glycerol to 200°C. The product was dissolved in boiling water, treated with animal charcoal and filtered while hot. On cooling, succinin separated as a colorless semi-solid mass.

Van Bemmelen<sup>18</sup> obtained a water-soluble syrup by heating equivalent proportions of succinic acid and mannite to 170°C. Cane sugar and succinic acid at 160°C. yielded a humus-like substance.

As a result of a series of investigations Callahan<sup>20</sup> concluded that 2 parts of succinic acid to 1 part of glycerol yielded the most satisfactory product. A greater proportion of acid renders the product too hard; less acid results in a soft sticky resin. For succinic acid the temperature of treatment is 200°C. The time of heating depends somewhat on the size of the batch, from 15 minutes to 3 hours being required. A solution of the soluble resin in acetone may be used as a varnish.

The resin from succinic acid and glycerol is tough and flexible whereas that from phthalic anhydride and glycerol is hard and has a tendency toward brittleness according to Callahan.<sup>20</sup> By combining succinic acid and phthalic anhydride with glycerol it was found possible to make a tougher resin than that from phthalic anhydride alone. When a mixture of 118.4 parts of phthalic anhydride (4/5 mol), 141.5 parts succinic acid (1 1/5 mols) and 184 parts glycerol is heated, the first stage is the formation of a viscous, acetone-soluble resin. Further heating causes it to become insoluble and infusible. If the temperature is too high in the final heating a vesiculated mass is formed, but at lower temperatures (85-150°C.) no bubbles appear and the resin is clear. A layer 1/10 inch thick be-

Mar. 25, 1933, to Eastman Kodak Co.; *Brit. Chem. Abs.*, B, 1934, 57. 1,3-Propylene glycol carbonate (b.p.<sub>12</sub> 110° with decomp.) has been prepared by reacting 1,3-propylene chlorohydrin with sodium carbonate. See G. Steinmig and M. Wittwer, U. S. P. 1,907,891, May 9, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3731.

<sup>17</sup> For the preparation of succinic acid by the electrolytic reduction of fumaric or maleic acid, see J. F. Norris and E. O. Cummings, U. S. P. 1,457,791, June 5, 1923; *Chem. Abs.*, 1923, 17, 3427.

<sup>18</sup> J. M. van Bemmelen, *J. prakt. Chem.*, 1856, (1) 69, 84; *Jahresberichte*, 1856, 608.

<sup>19</sup> A. Funaro and L. Danesi, *Gazz. chim. ital.*, 1880, 10, 58; *Jahresberichte*, 1880, 799; *Chem. Zentr.*, 1880, 336.

<sup>20</sup> J. M. van Bemmelen, *Jahresberichte*, 1858, 435.

<sup>21</sup> M. J. Callahan, U. S. P. 1,091,732, March 31, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 1878.

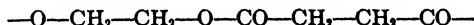
<sup>22</sup> M. J. Callahan, U. S. P. 1,108,332, Aug. 25, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 3506.

comes insoluble in 10 hours at 150°C. and forms a very tough product. Glycol succinate has been used in laminated glass.<sup>62</sup>

Arsem<sup>63</sup> made a mixed phthalic-succinic resin. He first prepared an intermediate resin from 1 mol of phthalic anhydride and 1 mol of glycerol and then combined succinic acid with this hydroxy-ester. A mixture of 184 parts of glycerol and 296 parts of phthalic anhydride is first heated at 200-210°C. until gas bubbles cease and 118 parts of succinic are then added to combine with the basic resin. The mixture finally is heated at 210-225°C. until it becomes jelly-like and, when cold, forms a brittle, hard, transparent mass. Arsem believed that this resin is not identical with one formed by heating a mixture of all three reactants in one step.

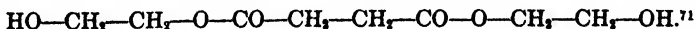
Downs and Weisberg<sup>64</sup> produced mixed resins containing succinic and malic, tartaric, maleic or fumaric acids. Like phthalic resins, these also exist in three forms: soluble (A), partially soluble-fusible (B) and insoluble, infusible, and water-resistant (C). To obtain the resin in the final form, the reacting materials are heated between 170° and 200°C. for about 20 hours, then below 135°C. for 10 hours or until the stage is passed where bubbles form in the resin, and finally the temperature is raised as high as 250°C. until the resin is water-resistant.

By the reaction between silver succinate and ethylene dibromide, Vorländer<sup>65</sup> obtained a microcrystalline powder which he considered to be the dimer of ethylene succinate. However, Carothers and Arvin<sup>66</sup> found the molecular weight of the material to vary between 1400 and 2000. The succinic ester of ethylene glycol may be prepared in various degrees of polymerization. These esters have been investigated by Carothers and Dorough,<sup>67</sup> who found that when prepared by the general method of heating the glycol and acid the products contained the group



to an extent varying between 6 and 23 structural units per molecule. These polymers are soluble in chloroform but insoluble in ether and benzene. The lower polymers are soluble in water. A still lower polymer, probably the dimer, was obtained by Tilicheiev<sup>68</sup> by distilling the higher polymers. The monomer is not known to exist.

Carothers and Hill<sup>69</sup> heated a sample of polyethylene succinate in a high vacuum and obtained a tough, horny, somewhat elastic residue. On heating to 97°C., it softened to a very viscous, slightly rubbery mass which could be drawn out into fibers. With excess glycol at 100°C. succinic acid forms the di-β-hydroxy-ethyl succinate,



The diacetyl derivative boils at 198° at 5 mm.

<sup>62</sup> H. C. Rohlf, U. S. P. 1,899,588, Feb. 28, 1933, to General Electric Co.; *Brit. Chem. Abs.* B, 1934, 62. For the employment of acids other than succinic acid, such as citric, adipic, pimelic and phthalic, in compound glass along with cellulose derivatives, see British P. 373,579, 1932, addn. to 363,933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3575. British P. 363,933, 1930; *Chem. Abs.*, 1933, 27, 1729 and British P. 363,940, 1930; *Chem. Abs.*, 1933, 27, 2771. See Chapters 47 and 49.

<sup>63</sup> W. C. Arsem, U. S. P. 1,098,776, June 2, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 2816 and British P. 24,234, 1912, to General Electric Co., Ltd.; *Chem. Abs.*, 1914, 8, 1243.

<sup>64</sup> C. R. Downs and L. Weisberg, U. S. P. 1,667,300, Apr. 24, 1928, to Barrett Co.; *Brit. Chem. Abs.* B, 1928, 419. British P. 173,225, 1921; *J.S.C.I.*, 1923, 42, 667A.

<sup>65</sup> D. Vorländer, *Ann.*, 1894, 280, 167; *Chem. Zentr.*, 1894, 2, 657.

<sup>66</sup> W. H. Carothers and J. A. Arvin, *J.A.C.S.*, 1929, 51, 2566.

<sup>67</sup> W. H. Carothers and G. L. Dorough, *J.A.C.S.*, 1930, 52, 711.

<sup>68</sup> M. Tilicheiev, *J. Russ. Phys.-Chem. Soc.*, 1925, 57, 143; *Chem. Abs.*, 1926, 20, 2823.

<sup>69</sup> J. W. Hill and W. H. Carothers, *J.A.C.S.*, 1933, 54, 1568.

<sup>71</sup> F. B. Shorland, *loc. cit.*

**Malic Acid.** Callahan<sup>72</sup> used malic acid and glycerol to produce a resin which could be used for molded insulation, or mixed with harder resins (phthalic glyceride) to make them tougher. In his process 134 parts malic acid and 92 parts glycerol are heated first to 110°C., ebullition occurs and the temperature is then raised gradually to 235°C., yielding a flexible and somewhat sticky resin. It is soluble in acetone and is fusible at approximately 100°C. Heating for a period of about 15 hours at a temperature below the fusing point but rising to 100°C. yields an infusible resin.

Protracted heat treatment is necessary if the resin from malic acid and glycerol is to be resistant to water. Downs and Weisberg<sup>73</sup> found that this resin and mixed resins containing malic and other dibasic acids could be rendered water-resistant to such an extent that a test sample submerged in boiling water for two minutes does not turn white. Heating the resin for about 30 hours at 170°C. is necessary.

Edible resins for use in making grease-proof wrapping paper for foodstuffs or as chicle substitutes in chewing-gum compositions are obtained from fruit acids such as malic or citric.<sup>74</sup> For example a mixture of 101 parts malic acid, 42 parts diethylene glycol and 24 parts glycerol is heated at 220-240°C., finally yielding a semi-elastic gel.

When malic acid is heated at 100°C. in air or in a vacuum, tribasic malomalic acid is formed from two molecules of malic acid. After fusing, the cold melt has a glass-like appearance.<sup>74</sup> Downs and Weisberg<sup>75</sup> have suggested the use of this acid in resins.

**Tartaric Acid.** In 1847 Berzelius,<sup>76</sup> on heating glycerol and tartaric acid to 150°C., obtained a soft mass which could be drawn out into threads. The product was deliquescent and could easily be hydrolyzed by water. Desplats<sup>77</sup> also studied the reaction between glycerol and tartaric acid.<sup>78</sup>

**Maleic and Fumaric Acids.**<sup>79</sup> Weisberg and Potter<sup>80</sup> heated maleic acid in the proportion of one mol of glycerol to one of acid. The acid dissolves forming a homogeneous mass and, as the heating is continued, the melting point gradually rises and the material, which at first is quite sticky and viscous, eventually loses its stickiness and becomes more solid when cold. At this stage the product is soluble in acetone, making a clear solution useful as a varnish. The time required to reach this point may vary according to the temperature at which the

<sup>72</sup> M. J. Callahan, U. S. P. 1,091,627, Mar. 31, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 1877. *British P.* 24,060, 1912; *Chem. Abs.*, 1914, 8, 1243.

<sup>73</sup> C. R. Downs and L. Weisberg, U. S. P. 1,667,199, Apr. 24, 1928, to Barrett Co.; *Chem. Abs.*, 1928, 22, 2072.

<sup>74a</sup> Carleton Ellis, U. S. P. 2,007,965, July 16, 1935, to Ellis-Foster Co.

<sup>74</sup> P. Walden, *Ber.*, 1899, 32, 2706. For further study of the effect of heat on malic acid see F. W. Morse, *J.A.C.S.*, 1929, 51, 1276.

<sup>75</sup> C. R. Downs and L. Weisberg, U. S. P. 1,667,198, Apr. 24, 1928, to Barrett Co.; *Chem. Abs.*, 1928, 22, 2072.

<sup>76</sup> J. Berzelius, *Rapport annuel*, 1847, 260; A. Wurtz, "Dictionnaire de Chimie," Paris, Librairie Hachette & Cie, 1870, I, (2), 1590.

<sup>77</sup> Desplats, *Compt. rend.*, 1859, 49, 216; A. Wurtz, *loc. cit.*

<sup>78</sup> For the oxidation of furfural to maleic and tartaric acids, see H. W. Witzel, U. S. P. 1,945,246, Jan. 30, 1934, to the Selden Co.; *Chem. Abs.*, 1934, 28, 2370. See also A. O. Jaeger, U. S. P. 1,945,354, Jan. 30, 1934, to the Selden Co.; *Chem. Abs.*, 1934, 28, 2366. J. Grolea and J. L. Weyler (*British P.* 123,712, 1918; *J.S.C.I.*, 1919, 38, 714A), made use of the neutral reaction products from tartaric acid (or citric) and various monohydric alcohols (n-butyl alcohol, isobutyl alcohol and isoamyl alcohol) in the making of dopes, lacquers, coatings and plastic films with acetone-soluble cellulose acetate. These esters yielded a transparent film which did not change under atmospheric influences.

<sup>79</sup> Among various processes for the preparation of maleic anhydride by the catalytic partial oxidation of benzene see, E. E. Punnett, U. S. P. 1,895,522, Jan. 21, 1933, to National Aniline & Chemical Co.; *Chem. Abs.*, 1933, 27, 2488. *British P.* 415,748, 1934; *Brit. Chem. Abs.*, B, 1935, 819. For the purification of maleic anhydride see C. Conover, U. S. P. 1,914,556, June 20, 1933, to Monsanto Chem. Works; *Chem. Abs.*, 1933, 27, 4248. See also C. R. Downs, *Ind. Eng. Chem.*, 1934, 26, 17. For diene synthesis see Chapter 40.

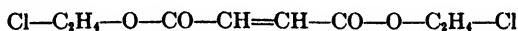
<sup>80</sup> L. Weisberg and R. S. Potter, U. S. P. 1,424,137, July 25, 1923, to Barrett Co.; *Chem. Abs.*, 1923, 16, 2219.



heating is conducted, the bulk of the batch and the rate of stirring. This resin is also soluble at room temperature in ethyl alcohol and ethyl acetate but less so than in acetone. It dissolves slightly in benzene. Cold water acts on it rapidly, causing it to become discolored and soft. If heating is continued at about 200°C., an exothermic reaction occurs with frothing, and the material becomes filled with bubbles. This frothy product may be rendered homogeneous by grinding and molding under heat and pressure. A bubble-free product may be obtained directly, however, by heating at a temperature at or near the melting point of the A-stage resin; the maximum temperature below 135°C. and may be as low as 90°C. or lower. For example, a batch of two pounds may be converted at 135°C. in about ten hours from the A-stage resin to the B-stage. This B-stage resin is insoluble in acetone, ethyl alcohol, and ethyl acetate, but on standing in contact with any of these materials for a considerable time, the finely powdered resin swells and forms a jelly-like mass. Heated for about 30 hours longer the resin reaches the C-stage.

On attempting the preparation of ethylene fumarate and maleate the formation of resins was observed by Vorländer.<sup>81</sup> Silver fumarate gave with ethylene dibromide a crystalline, apparently polymeric product which was transformed on heating into a transparent, infusible and very insoluble glass. The original "ethylene fumarate" was slowly dissolved by alkali, and added on bromine to give polymeric ethylene dibromosuccinate as a gummy mass, solidifying to an amorphous substance. From silver maleate with ethylene dibromide the corresponding ester was also obtained as a viscous gum, solidifying to a glass at low temperatures. Heated at 150-160°C. it was transformed into a rubber-like substance.

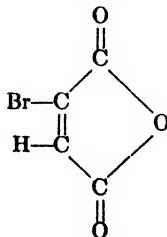
Vorländer likewise obtained resinous products on removal of chlorine from di(chloroethyl) fumarate,



by silver.

Fumaric acid also forms resins with polyhydric alcohols.<sup>82</sup> This acid behaves very much like maleic in its reaction with glycerol except that having a higher melting point, the first step is usually carried out at a higher temperature.

Zwilmeyer<sup>83</sup> has made use of halogenated acids in the preparation of the alkyd resins. The method of carrying out the preparation is as follows: a mixture of 183 parts of glycerol and 355 parts of monobromo-maleic anhydride

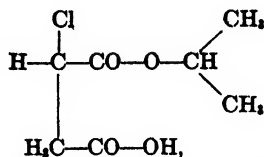


is slowly heated with stirring while a general increase in viscosity takes place. When gas evolution ceases, 430 parts of the mono-isopropyl ester of monochloro-succinic acid,

<sup>81</sup> D. Vorländer, *Ann.*, 1894, 280, 171; *Chem. Zentr.*, 1894, 2, 657; Beilstein, 4th Ed., 1920, II, 752.

<sup>82</sup> C. R. Downs and L. Weisberg, U. S. P. 1,067,197, Apr. 24, 1923, to the Barrett Co.; *Chem. Abs.*, 1923, 22, 2072.

<sup>83</sup> F. Zwilmeyer, U. S. P. 1,950,468, Mar. 13, 1934, to National Aniline & Chem. Co., Inc.; *Chem. Abs.*, 1934, 28, 3255.



are added. The resulting mixture is heated to 180-290°C. to yield a resinous material of very high elasticity. The mono-isopropyl ester of monochlorosuccinic acid is prepared by heating maleic anhydride and isopropyl alcohol in the presence of hydrogen chloride and separating with alkali the mono-acid salt.

In place of the mono-isopropyl chlorosuccinate, 145 parts of acrylic acid may be added<sup>84</sup> and the mixture heated to 180-200°C. to produce a hard, brittle resin soluble in acetone and in diethyl phthalate.

**Citric Acid.** Experiments by van Bemmelen<sup>85</sup> yielded a product which he termed citrin. One equivalent of citric acid heated at 160°C. with an excess of glycerol yielded a syrupy product which after several hours heating at 160-170°C. became very hard, tough, brownish-yellow, porous and difficult to pulverize. Even at 200°C. the material exhibited approximately the same consistency as at room temperature. On exposure to air the sample grew softer. It was insoluble in water, alcohol and ether and when allowed to stand in cold water for a long time produced no acid reaction. When boiled with alcohol and water it became a thick syrup. One equivalent of citric acid with approximately two equivalents of glycerol heated for several hours to 170°C. yielded citro-diglycerol. One equivalent each of citric acid and glycerol heated for 20 hours at 160°C. yielded a very hard, light yellow, transparent resin, which adhered tenaciously to the glass of the vessel in which it had been prepared and could not readily be separated. This was much harder than citro-diglycerol and did not soften in the air. In hot and cold water very little action was noticed. It was soluble in concentrated hydrochloric acid and dissolved in sulphuric acid with blackening. Van Bemmelen considered this product to be citro-monoglycerol. He summarized the reaction between citric acid and glycerol in this manner: at 100-120°C. a syrup is formed and water is evolved, between 100-200°C. the syrup grows thicker and, after longer heating and the loss of 4 to 6 equivalents of water, this changes to a solid neutral insoluble substance.

Lourenço<sup>86</sup> heated citric acid and glycerol to 160°C. obtaining a gummy, water-soluble body. Heating to 215°C. resulted in a hard, brittle product, insoluble in water. At 140°C. equivalent quantities of mannite and citric acid yielded a hard yellowish, tasteless substance insoluble in water, alcohol or ether.<sup>87</sup>

Callahan,<sup>88</sup> on heating 1.5 parts of citric acid and 1 part of glycerol at a temperature of 160°C., formed a resin which was hard and strong but which did not have the flexibility desired for impregnating paper or cloth for electrical insulation. The addition of certain substances, specifically, meta-dinitrobenzene, ethyl benzoate, acetanilide and  $\beta$ -naphthol, promotes flexibility of the citric acid resin according to Dawson.<sup>89</sup> To a mixture of 11.4 parts of citric acid, 5 parts of glycerol and 5 parts of methyl alcohol are added from 1 to 10 parts of the plas-

<sup>84</sup> F. Zwilgmeyer, U. S. P. 1,975,246, Oct. 2, 1934, to National Aniline & Chemical Co., Inc.; *Chem. Abs.*, 1934, 28, 7563.

<sup>85</sup> J. M. van Bemmelen, *J. prakt. Chem.*, 1856, (1) 69, 93; *Jahresberichte*, 1856, 603.

<sup>86</sup> M. A. von Lourenço, *Ann. chim. phys.*, 1863, (3) 67, 312.

<sup>87</sup> H. Debus, *Phil. Mag.*, 1844 (4), 16, 438. See J. M. van Bemmelen, *Jahresberichte d. Chem.*, 1856, 424. L. Gmelin, "Handbook of Chemistry," Translation by H. Watts, Cavendish Society, London, 1869, XIII, 462.

<sup>88</sup> M. J. Callahan, U. S. P. 1,001,723, Mar. 31, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 1278.

<sup>89</sup> E. S. Dawson, Jr., U. S. P. 1,065,112, Jan. 27, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 1215.

ticizing agent. Articles to be impregnated are dipped into the solution and baked at 125°C. to drive out the alcohol and to start the reaction which is completed at 150-200°C. The resin obtained from citric acid and glycerol at low temperature lacks water-resistance. Reaction at high temperature (180-200°C.) lessens the hygroscopicity of the product but at the same time causes a deepening in the color. By adding an appropriate dye (methyl violet 2B)<sup>90</sup> to the resin before it becomes infusible and insoluble, a colored product is first obtained. On heat treatment, the color developed during resin-decomposition is neutralized by the dye and a water-white product results. The proportions of the various constituents used are as follows: 200 g. of citric acid (crystals), 100 g. of glycerol and 8 cc. of a 0.1 per cent aqueous solution of methyl violet 2B.<sup>91</sup>

The product obtained by treating citric glyceride with acetic or benzoic anhydride is water-soluble. A mixture of glycerol and aconitic acid forms an elastic resin.<sup>92</sup>

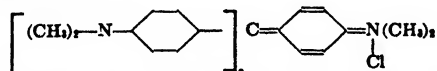
Sager<sup>93</sup> recommended as a ground-joint lubricant the resin obtained by heating 1 mol of citric acid and 1.5 mols tetraethylene glycol at 180°C. for 1.5 hours. It is insoluble in both aromatic and aliphatic hydrocarbons but is soluble in water, alcohol and acetone.

**Adipic Acid.**  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$ . A process for making adipic acid and its homologues consists in the oxidation of hydroaromatic alcohols produced by the hydrogenation of phenols. The oxidation may be carried out with nitric acid in the presence of an oxidizing catalyst (vanadium or molybdenum oxide or compounds such as ammonium vanadate)<sup>94</sup> at a temperature of 50-60°C. Homologues may also be obtained by this means:  $\alpha,\beta$ -dimethyl adipic acid (2,3-dimethyl hexanedioic acid) is produced by oxidizing 1,3,5-hexahydro-xylenol.<sup>95</sup>

The adipic esters can be used as softening agents in the celluloid, lacquer, and film industries.<sup>96</sup> Heating the esters of adipic acid with polyhydric alcohols yields gum-like, hard products, which have been suggested as rubber substitutes.<sup>97</sup>

Differing from the glycerol-phthalic anhydride resins, which become hard and brittle at high temperatures, those formed from glycerol and adipic acid or other straight-chain dibasic acids (pimelic, suberic, azelaic or sebacic) are permanently soft, rubbery and plastic. There are three stages in their formation, as in other resins of this class. In the A stage they are syrupy liquids, soluble in acetone; in the B stage they are soft and rubbery and soluble in acetone but insoluble in benzene and in the C stage they are soft and rubbery but insoluble in the common organic solvents. One mol glycerol and  $1\frac{1}{2}$  mols adipic acid are heated at 165-170°C. for 1 to 5 hours to yield a resin in the A stage which sets to a firm jelly

<sup>90</sup> Methyl violet 2B has the structure



<sup>91</sup> O. A. Cherry, U. S. P. 1,983,668, Dec. 11, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 854.

<sup>92</sup> T. Habu, Japanese P. 93,028 and 93,029, 1931; *Chem. Abs.*, 1932, 26, 4488.

<sup>93</sup> T. P. Sager, *Ind. Eng. Chem. (Anal. Edit.)*, 1932, 4, 388.

<sup>94</sup> For the use of copper, cerium, manganese, lead, iron, chromium, cobalt, nickel, tungsten, tellurium, bismuth, calcium, magnesium, uranium, barium, silver, molybdenum, vanadium or mercury compounds in the oxidation of cyclohexanol and cyclohexanone to adipic acid, see R. P. Perkins and A. J. Dietsler, U. S. P. 1,960,211, May 22, 1934, to Dow Chemical Co.; *Chem. Abs.*, 1934, 28, 4435.

<sup>95</sup> W. Schrauth, U. S. P. 1,921,101, Aug. 8, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5084.

<sup>96</sup> Esters such as bornyl adipate, cyclohexyl hydrophthalate and cyclohexyl benzoate have also been suggested for use as vulcanization accelerators. (British P. 339,336, 1930, to Deutsche Hydrierwerke A.-G.; *Brit. Chem. Abs. B*, 1931, 264.)

<sup>97</sup> W. Schrauth, *Chem. Ztg.*, 1929, 53, 41; *Brit. Chem. Abs. B*, 1929, 163. See *J.S.C.I.*, 1929, 48, 95.

on cooling. Further heating for  $4\frac{3}{4}$  hours gives the B stage and in a half hour more the C stage.<sup>99</sup>

Synthetic resins are also prepared by condensing adipic acid homologues containing a branched chain with a polyhydric alcohol. These products, which are very plastic and which may be added to phthalic glyceride to produce flexibility, are made by heating a mixture of isomeric methyladipic acids with glycerol and boric acid at  $160^{\circ}\text{C}$ .<sup>100</sup> Vulcanizable mixtures are obtained by adding the elastic, factice-like glycerol ester of methyladipic acid to rubber.<sup>100</sup> When adipic acid is first condensed with triethanolamine it gives an alcohol-soluble product. On further heating this is converted into an insoluble gummy, elastic and gelatinous material which likewise finds use as a softening agent for synthetic and natural resins, and as a vulcanization accelerator.<sup>101</sup>

Adipic esters of the dihydric alcohols form tallowy or butter-like masses. The glycol ester may be prepared by mixing a solution of ethylene glycol and pyridine in pinacolone with a similar solution of the dichloride of adipic acid, or by the action of ethylene dibromide on potassium adipate. The propylene glycol ester is similarly obtained.  $\alpha$ -Methyladipic acid and ethylene oxide react to give a brownish waxy mass.<sup>102</sup> With excess glycol at  $100^{\circ}\text{C}$ . adipic acid forms the di- $\beta$ -hydroxyethyl adipate (b.p.  $210^{\circ}\text{C}$ . at 5 mm.).<sup>102</sup>

**Azelaic Acid.**  $\text{HOOC}(\text{CH}_2)_7\text{COOH}$ . The oxidation of unsaturated oils yields azelaic acid as one of the products. This acid may be condensed with glycerol to form a plastic material<sup>103</sup> recommended for making lacquers or as a binder in linoleum.<sup>103</sup> When azelaic acid is replaced by acids having a longer carbon-chain the products are more flexible.<sup>103</sup>

**Sebacic Acid.**  $\text{HOOC}(\text{CH}_2)_9\text{COOH}$ .<sup>107</sup> Berthelot<sup>108</sup> reacted sebacic acid with glycerol at  $200^{\circ}\text{C}$ . and isolated from the product a small quantity of neutral crystalline compound which he called sebin.

Bruson<sup>109</sup> heated 1 mol of glycerol and 1.5 mol of sebacic acid at  $170^{\circ}\text{C}$ . until a test sample was a firm jelly when cold. At this stage the product is soluble and may be used as a plasticizer for nitrocellulose in coatings for fabrics,<sup>110</sup> or for rubber articles.<sup>111</sup> Further heating renders the mass insoluble but it is still soft and pliant.

The glycol ester was prepared by Carothers and Hill<sup>112</sup> by heating a mixture of sebacic acid and a slight excess of glycol. The product was a hard wax which when softened by heating could be drawn out to transparent fibers.

The resin obtained from sebacic acid and glycerol has been used as a cement

<sup>99</sup> H. A. Bruson, U. S. P. 1,779,367, Oct. 21, 1930, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1931, 25, 177. British P. 341,477, 1929, to Chem. Fabr. Dr. K. Albert G.m.b.H.; *Brit. Chem. Abs. B.*, 1931, 453.

<sup>100</sup> British P. 328,728, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5518.

<sup>101</sup> German P. 555,586, 1929, to Deutsche Hydrierwerke A.-G.; *Chem. Abs.*, 1932, 26, 6183.

<sup>102</sup> British P. 376,929, 1932, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1933, 27, 4111.

<sup>103</sup> German P. 318,322, 1917, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1920, 39, 427A.

<sup>104</sup> F. B. Shorland, *loc. cit.*

<sup>105</sup> British P. 377,366, 1931, to Deutsche Gasglühlicht-Auer-Ges.m.b.H.; *Brit. Chem. Abs. B.*, 1932, 948. French P. 715,584, 1931; *Chem. Abs.*, 1932, 26, 2025.

<sup>106</sup> British P. 348,563, 1929, to Deutsche Gasglühlicht-Auer-Ges.m.b.H.; *Chem. Abs.*, 1932, 26, 5221. French P. 688,962, 1930; *Chem. Abs.*, 1931, 25, 1046.

<sup>107</sup> French P. 40,924, 1931, addn. to 688,962, to Deutsche Gasglühlicht-Auer-Ges.; *Chem. Abs.*, 1933, 27, 1464.

<sup>108</sup> According to Ishiguro (*J. Rubber Soc. [Japan]*, 1930, 2, 238; *Brit. Chem. Abs. B.*, 1931, 1106), sebacic acid is a better softening agent for rubber than is stearic acid.

<sup>109</sup> M. M. Berthelot, *Ann. chim. phys.*, 1854, (3) 41, 293.

<sup>110</sup> H. A. Bruson, U. S. P. 1,779,367, Oct. 21, 1930, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1931, 25, 177. British P. 341,477, 1929, to Chem. Fabr. Dr. K. Albert G.m.b.H.; *Brit. Chem. Abs. B.*, 1931, 453.

<sup>111</sup> H. A. Bruson, U. S. P. 1,761,813, June 3, 1930, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1930, 24, 3682.

<sup>112</sup> H. A. Bruson, U. S. P. 1,761,814, June 3, 1930, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1930, 24, 3683.

<sup>113</sup> W. H. Carothers and J. W. Hill, *J.A.C.S.*, 1932, 54, 1566.

in laminated glass.<sup>114</sup> Resins of this type when used as binders in safety glass have a high holding power. They do not become brittle on exposure to light and maintain their strength and resilience after a long period of use.

With an excess of glycol, sebacic acid reacts at 110-115°C. to yield the di- $\beta$ -hydroxyethyl sebacate of m.p. 46°. On heating to 160°, the ester slowly polymerizes. The diacetyl derivative



boils at 242°C. at 5 mm.<sup>114</sup>

**Camphoric Acid.**  $\text{C}_8\text{H}_{14}(\text{COOH})_2$ . Heated to 200°C. in a sealed tube with glycerol, camphoric acid forms a viscous, neutral mass that Berthelot<sup>115</sup> called camphorin. Callahan<sup>116</sup> also studied its reaction with glycerol. He heated 46 parts of glycerol and 100 parts of camphoric acid to 100°C. whereupon the mixture became uniform in appearance. The temperature was then slowly raised to 250°C. The resinous product is soluble in acetone, slightly soluble in methyl and ethyl alcohol and insoluble in benzene. It is clear, yellow, melts at 110-130°C. and may be hardened by heating for some time at 90-135°C.

#### BORIC ACID

Glycol and glyceryl borates and boriborates are water-soluble resins. They are compatible with nitrocellulose and with gelatin. Glycol boriborate<sup>117</sup> has been used for the lubrication of dyed cotton previous to spinning; it is waxy, hygroscopic, non-corrosive, non-inflammable and water-soluble.<sup>118</sup> By heating to 100°C. 150 parts of diethylene glycol and 70 parts of boric acid together with 80 parts of borax with agitation, combination takes place and, as the temperature is raised from 120-130°C., water is evolved. The resin obtained is a viscous syrup of high molecular weight, tasteless, odorless and of a light amber color or colorless. The resin, moreover, is soluble in water and it is practically neutral, non-corrosive, non-toxic and antiseptic. When heated above 275°C. the product loses water and becomes harder and non-tacky; if heated further, a water-soluble glass is obtained which goes into solution very slowly but which is extremely hygroscopic. It is particularly adaptable as a plasticizer for glues, gelatin, gum arabic, tragacanth or karaya and as a base for cosmetical and pharmaceutical preparations. Dissolved in methyl alcohol or in glycol ethers, it can be used as a special adhesive for glassine, cellophane or celluloid.<sup>119</sup>

The method of refining oils and fats by treatment with anhydrous boric acid<sup>120</sup> has been extended to the use of the boric acid esters of polyhydric alcohols.<sup>121</sup> Moreover, the polyhydric alcohols can be condensed with phthalic anhydride in the presence of boric acid by heating to 250°C. A glycerol-boric ester is used in the preparation of mucilage,<sup>122</sup> and a viscous composition suggested for electrolytic condensers is obtained by the reaction of ethylene glycol with ammonium borate and boric acid.<sup>123</sup>

<sup>114</sup> J. C. Zola, U. S. P. 1,900,536, Mar. 7, 1933, to Duplate Corp.; *Brit. Chem. Abs. B*, 1934, 96. See Chapter 47.

<sup>115</sup> F. B. Shorland, *loc. cit.*

<sup>116</sup> M. M. Berthelot, *Compt. rend.*, 1853, 37, 398.

<sup>117</sup> M. J. Callahan, U. S. P. 1,091,628, Mar. 31, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 1878. *British P.* 24,059, 1912; *Chem. Abs.*, 1914, 8, 1243.

<sup>118</sup> Known as Aquarexin GM.

<sup>119</sup> C. B. Ordway, *Rayon and Melliand Text. Month.*, 1934, 15, 18; *Brit. Chem. Abs. B*, 1934, 359; *Am. Dyestuff Repr.*, 1935, 22, 638; *Chem. Abs.*, 1934, 28, 4230.

<sup>120</sup> H. Bennett, U. S. P. 1,953,741, Apr. 3, 1934; *Chem. Abs.*, 1934, 28, 5849.

<sup>121</sup> Cf. M. Schellmann and H. Fransen, *German P.* 569,797, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3241.

<sup>122</sup> M. Schellmann, *German P.* 592,059, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3209.

<sup>123</sup> *British P.* 405,398, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1934, 286.

<sup>124</sup> S. Ruben, *Canadian P.* 330,058, 1933, to the Ruben Condenser Co.; *Chem. Abs.*, 1933, 27, 2100.

## ETHER-ACIDS

Resins for moldings or for coatings are formed by the reaction of polyhydric alcohols and ether-carboxylic<sup>124</sup> or thioether-carboxylic<sup>125</sup> acids (diglycolic, methylhydracrylic, salicylacetic, thiodiglycolic, thiodilactylic and 2-carboxyphenylthioglycolic acids or anhydrides). For example, diglycolic acid, heated with glycerol to a final temperature of about 140°C., yields a colorless product having the consistency of honey, which on heating in a thin layer at 160°C. for several hours gives a solid film. These hardened condensation products are good electrical insulators and are very elastic and pliable. They are recommended as coatings for wire, wire fabrics<sup>126</sup> and other metallic parts<sup>127</sup> of electrical machinery, or they can be mixed with fibrous fillers and molded under pressure.<sup>128</sup>

## KETONE-ACIDS

Acids of this class, which have been used to form resins by reaction with polyhydric alcohols, include benzoylbenzoic, toluylbenzoic, and benzophenone-2,4'-dicarboxylic acids.

Downs and Weisberg<sup>129</sup> heated benzoylbenzoic acid with glycerol to produce a hard resin unaffected by water. Polybasic acids may replace part of the benzoylbenzoic acid. Ellis<sup>130</sup> found that a mixture of 120 parts of toluylbenzoic acid and 15.5 parts of glycerol, heated for half an hour to a temperature of 290°C. in an aluminum vessel equipped with a short air-cooled condenser, yields a hard resin of acid number 23.4. This resin is compatible with cellulose acetate. Benzoylbenzoic acid treated in the same way yields a resin whose acid number is 19.3.

Hahn<sup>131</sup> incorporated benzoylbenzoic glyceride with cellulose acetate in a lacquer. One formula suggested is 12 parts of cellulose acetate, 3 parts resin, 6 parts of softener and 79 parts of solvent.<sup>132</sup> Other esters of benzoylbenzoic acid (propyl, butyl, isoamyl) have been suggested as plasticizers for cellulose nitrate and acetate.<sup>133</sup>

Benzoylbenzoic, toluylbenzoic, chlorbenzoylbenzoic and similar acids, formed by the action of aromatic hydrocarbons or hydrocarbon derivatives on phthalic anhydride in the presence of aluminum chloride, are monobasic acids. The resins obtained by their reaction with glycerol can hardly be considered to have the complexity of the resins formed from dibasic acids. It is even doubtful if they

<sup>124</sup> K. Schumann, E. Münch and O. Schlichting, German P. 534,215, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 814. British P. 327,722, 1928; *Chem. Abs.*, 1930, 24, 5173. French P. 685,565, 1929; *Chem. Abs.*, 1930, 24, 6041.

<sup>125</sup> E. Münch and G. Kraemer, German P. 538,831, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2025. Addn. to German P. 534,215.

<sup>126</sup> British P. 331,203, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 915. French P. 689,104, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1108.

<sup>127</sup> French P. 694,425, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1926.

<sup>128</sup> French P. 694,944, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1957.

<sup>129</sup> C. R. Downs and L. Weisberg, U. S. P. 1,667,197, Apr. 24, 1928, to Barrett Co.; *Chem. Abs.*, 1928, 22, 2072.

<sup>130</sup> Carleton Ellis, U. S. P. 1,886,242, Nov. 1, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 1530.

<sup>131</sup> F. C. Hahn, Canadian P. 312,568, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1931, 25, 4422. British P. 316,321, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 1754.

<sup>132</sup> A. O. Jaeger used the alkyl esters of acids of this type, such as butyl benzoylbenzoate, methyl benzoylacrylate and butyl naphthoylbenzoate as plasticizers for resins. See A. O. Jaeger, U. S. P. 1,978,710, Oct. 30, 1934, to American Cyanamid & Chemicals Corp.; *Chem. Abs.*, 1935, 29, 253. French P. 703,018, 1930, to Selden Co.; *Chem. Abs.*, 1931, 25, 4423. British P. 359,164, 1929; *Chem. Abs.*, 1932, 26, 4969. H. J. West (U. S. P. 1,809,614, June 9, 1931, to Selden Co.; *Chem. Abs.*, 1931, 25, 4828) recommended butyl benzoylbenzoate for use in high-vacuum pumps.

<sup>133</sup> H. A. Bruson, U. S. P. 1,909,092, May 16, 1933, to American Cyanamid Co.; *Brit. Chem. Abs. B*, 1934, 37.

can be considered polymeric in the same sense. Their resinous nature is more probably the result of their slowness of crystallization. Toluylbenzoic acid can be fused to form a melt which remains glassy for a long time.<sup>134</sup>

Benzophenone-2,4'-dicarboxylic acid is insoluble in water and does not sublime when heated, properties of importance in resin production. Resins made from this acid are resistant to water and no loss of acid occurs in their formation. Bruson<sup>135</sup> heated a mixture of 270 parts benzophenonedicarboxylic acid and 62 parts glycerol in a kettle equipped with an agitator and after heating for about 5 hours at 190-200°C., obtained a hard resin readily soluble in acetone. After 8 or 10 hours at this temperature the resin reverts into an insoluble and infusible form. Ethylene glycol and benzophenone-2,4'-dicarboxylic acid yield a hard, brittle, pale resin soluble in butyl acetate or acetone. If pentaerythritol is used, the resin becomes insoluble and infusible after only 3 or 4 hours at 180-190°C.

Another group of polybasic acids includes the products obtained by treating maleic anhydride with compounds containing conjugated double bonds and capable of forming simple adducts according to the diene synthesis.<sup>136</sup>

Such compounds as vinyl acetate, styrene, indene and acrylic esters react with maleic anhydride when heated in the presence of a catalyst like benzoyl peroxide to form polymeric polybasic acids.<sup>137</sup> These products may be heated with glycerol to yield resins or the glycerol may be added before polymerization.<sup>138</sup> For example, a mixture of styrene, maleic anhydride and glycerol, heated in an autoclave to 120°C., yields a resin insoluble in alkalis or in organic solvents.

#### POLYHYDRIC ALCOHOLS

Being the most generally available polyhydric alcohol, glycerol has been more widely used than any other alcohol of this type to form resins by reaction with polybasic acids. In certain instances the glycerol is replaced by an acid glyceride such as triacetin. The acid under these conditions is volatilized at the temperature of the reaction.<sup>139</sup>

Other alcohols than glycerol include polyglycerol, the glycols and polyglycols, pentaerythritol, sorbitol<sup>140</sup> and mannitol. Different polyhydric alcohols usually yield different products with the same polybasic acid. When heated for a sufficiently long time with either a dibasic acid or a more highly carboxylated compound, glycerol forms an insoluble, infusible mass. Polyhydric alcohols containing more than three hydroxyl groups form this kind of material even more readily than glycerol. On the other hand glycols (containing only two hydroxyl groups) react with dibasic acids to form permanently fusible bodies, but with acids containing more than two carboxyl groups they may be expected to yield insoluble bodies. The complexity of the reactants thus forms the basis for classifying sim-

<sup>134</sup> Cf. Chapter 4, especially the work of D. Vorländer.

<sup>135</sup> H. A. Bruson, U. S. P. 1,813,838, July 7, 1931, to Röhm & Haas Co.; *Chem. Abs.*, 1931, 25, 5305. U. S. P. 1,807,503, May 26, 1931; *Chem. Abs.*, 1931, 25, 4139. See German P. 562,954, 1933, to Chem. Fabr. Kurt Albert G.m.b.H.; *Chem. Abs.*, 1934, 28, 919.

<sup>136</sup> See Chapter 40.

<sup>137</sup> British P. 376,479, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 948.

<sup>138</sup> British P. 376,481, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 948. See A. Voss and E. Dickhäuser, German P. 544,328, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2609. Addn. to German P. 549,101, 1930; *Chem. Abs.*, 1932, 26, 1818.

<sup>139</sup> R. Weithöner, British P. 395,894, 1932, to Glasurit-Werke M. Winkelman A.-G.; *Brit. Chem. Abs.* B, 1933, 837. French P. 743,027, 1933; *Chem. Abs.*, 1933, 27, 3837. German P. 590,636, 1934; *Chem. Abs.*, 1934, 28, 3256.

<sup>140</sup> H. H. Strain (*J.A.C.S.*, 1934, 56, 1756) has found that the rare sugar alcohol d-sorbitol occurs in large quantities (2.4-2.7 per cent) in Toyon berries (the fruits of *Photinia arbutifolia*, Lindl.) and may be isolated by extraction with boiling water or with ethanol, followed by fermentation and recrystallization. When ethanol is used, fermentation apparently is not necessary and the sorbitol may be directly recrystallized from pyridine.

TABLE 44.—Polyhydric Alcohols.

Glycol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$
Polyglycols	$\text{HO}-(\text{CH}_2-\text{CH}_2-\text{O})_n-\text{H}$
Propane-1,2-diol	$\text{HO}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$
Trimethylene glycol	$\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$
Butane-2,3-diol	$\text{CH}_3-\text{CHOH}-\text{CHOH}-\text{CH}_3$
Glycerol	$\text{HO}-\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{OH}$
Polyglycerols	$\text{HO}-(\text{CH}_2-\text{CHOH}-\text{CH}_2-\text{O})_n-\text{H}$
Pentaerythritol	$\begin{array}{c} \text{HO}-\text{CH}_2 \qquad \text{CH}_2\text{OH} \\ \qquad \diagdown \quad \diagup \\ \qquad \text{C} \\ \qquad \diagup \quad \diagdown \\ \text{HO}-\text{CH}_2 \qquad \text{CH}_2\text{OH} \end{array}$
Hexitols (Sorbitol and Mannitol)	$\text{HO}-\text{CH}_2-(\text{CHOH})_4-\text{CH}_2-\text{OH}$
Hexahydroxycyclohexane	$\begin{array}{ccccc} & \text{H} & & \text{H} & \\ &   & &   & \\ \text{H} & \text{C} & - & \text{C} & \text{H} \\ &   & &   & \\ & \text{OH} & & \text{OH} & \\ \text{H} & \text{C} & - & \text{C} & \text{H} \\ &   & &   & \\ \text{HO} & \text{C} & - & \text{C} & \text{OH} \\ &   & &   & \\ & \text{OH} & & \text{OH} & \end{array}$

ple polyhydric alcohol-polybasic acid resins into heat-convertible and heat-non-convertible resins as proposed by Kienle and Ferguson.<sup>141</sup>

#### POLYGLYCEROL

Polyhydric alcohols generally can be condensed with themselves to yield complex bodies retaining an alcoholic character.<sup>142</sup> When glycerol is distilled the residue in the still contains di- and triglycerol, the mixture being called "polyglycerols."<sup>143</sup> They are formed by the elimination of water between two or more molecules of glycerol. By heating glycerol for a half hour at 280°C. in the presence of 0.5 per cent of sodium hydroxide (or acetate) the greater part of the glycerol is converted into the condensation product. This condensed glycerol reacts more rapidly with organic acids than normal glycerol and its use facilitates resinification. The initial fusible or class A resin is formed in about one-fifth the time required

<sup>141</sup> R. H. Kienle and C. S. Ferguson, *Ind. Eng. Chem.*, 1929, 21, 349. See also R. H. Kienle, *ibid.*, 1930, 22, 590. See Chapter 41.

<sup>142</sup> The formation of polyglycerols is discussed by E. Leurs (*J.S.C.I.*, 1922, 41, 97T), by A. Rayner (*ibid.*, 224T) and by M. Rangier (*Compt. rend.*, 1923, 187, 345; *Chem. Abs.*, 1923, 22, 4458). R. I. Bashford heats glycerol with zinc chloride (U. S. P. 1,467,299, Sept. 11, 1923, to Grasselli Powder Co.; *Chem. Abs.*, 1923, 17, 3680). Diglycerol is obtained by heating glycerol with thorium or magnesium oxide and with or without sodium silicate (British P. 265,146 and 265,147, 1926, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1926, 22, 244. H. Weber and F. Niemeyer, German P. 494,430 and 494,431, 1926, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1930, 24, 3760). Passing inert gases through glycerol which is heated with sodium acetate yields diglycerol. (British P. 264,800, 1926, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1926, 22, 244.) S. N. Ushakov and E. M. Obryadina, *Plast. Massui*, 1932, (1) 19; *Chimie et industrie*, 1933, 29, 1418; *Chem. Abs.*, 1933, 27, 4426; *Ind. Eng. Chem.*, 1933, 25, 997, state the most efficient catalysts for direct polymerisation of glycerol by heat are sulphuric acid, sulphurous acid, sulphates and sulphites, particularly mercuric and cupric sulphates. By refluxing glycerol for 4 hours in the presence of 4 per cent catalyst, condensation occurs to the extent of 60-68 per cent. The product is dark-brown, viscous and soluble in water, alcohol, acetone and in alcoholic benzene. Further heating results in an infusible material which can form elastic films. Purification by steam distillation yields 31-50 per cent of a dark brown secondary resin which is insoluble in water and corresponds to the structural formula  $(\text{C}_3\text{H}_5\text{O}_2)_n$ . See Chapters 24 and 50.

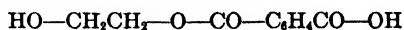
<sup>143</sup> For the cyclic ethers formed by autocondensation of glycerol and their use as plasticisers for cellulose derivatives, see H. Dreyfus, French P. 745,040, 1933; *Chem. Abs.*, 1933, 27, 4428. O. Mers (*Farben-Chem.*, 1934, 5, 91; *Brit. Chem. Abs. B*, 1934, 616) has considered the glycerol ethers as solvents, especially their miscibility with common varnish solvents and thinners, the solvent power for nitro-cellulose, for acetyl cellulose and for natural and synthetic resins. For the action of heat and glycerol on nitrocellulose and for the manner in which the viscosity of the latter is lowered, see M. G. Milliken, U. S. P. 1,967,180, May 1, 1934, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 4231.



with glycerol. The physical properties of the polyglycerol resins do not differ greatly from those made from normal glycerol.<sup>144</sup>

## GLYCOLS

When equimolecular amounts of phthalic anhydride and ethylene glycol are heated together to 140-160°C., the monoester



is first formed by direct addition of the reactants. This compound can be obtained in the form of crystals. Further heating causes an increase in the molecular weight by union of a large number of molecules of the initial simple ester. The viscosity of the heated mass increases but the product remains fusible at all stages.<sup>145</sup> It is compatible with both nitrocellulose and cellulose acetate.<sup>146</sup> Glycol-phthalic anhydride resin has been recommended as a cement for high-vacuum work<sup>147</sup> and has been suggested for impregnating paper and for the manufacture of lacquers.<sup>148</sup> The ethylene glycol phthalate can be prepared by using as catalysts such substances as sulphuric acid,<sup>149</sup> basic cuprous carbonate, bismuth subcarbonate, the carbonates of cobalt, lithium, manganese, cadmium and barium, and the nitrates of calcium, beryllium,

<sup>144</sup> See L. Weisberg and R. S. Potter, U. S. P. 1,424,137, July 25, 1922, to the Barrett Co.; *Chem. Abs.*, 1922, 16, 3219. See also F. Groff, U. S. P. 2,008,417, July 16, 1935, to Bakelite Corp.

<sup>145</sup> H. Hönel, *Kunststoffe*, 1931, 35, 76, 105, 132; *Chem. Abs.*, 1931, 25, 5047.

<sup>146</sup> H. E. Hofmann and E. W. Reid, *Ind. Eng. Chem.*, 1929, 21, 964. The soft nature of the esters of glycol and polyglycols makes them valuable as plasticizers for cellulose esters. O. Loehr reacts polyglycols with benzoic acid and obtains a high-boiling viscous liquid which he mixes with cellulose nitrate or acetate to form flexible lacquers. (U. S. P. 1,783,176, Dec. 2, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 414. Canadian P. 285,919, 1923; *Chem. Abs.*, 1929, 23, 1267.) O. Loehr also uses the benzoates of polyethylene glycol monoethyl ethers (U. S. P. 1,865,196, June 28, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4487). Such mixed esters of diethylene glycol as the butyrate-laurate have been suggested for the same purpose (R. Calvert, U. S. P. 1,807,304, May 26, 1931, to Van Schaack Bros. Chemical Works, Inc.; *Chem. Abs.*, 1931, 25, 4090). Other phthalic esters which have been mentioned for use as cellulose ester plasticizers are: dibenzyl phthalate (R. H. Van Schaack, Jr., U. S. P. 1,734,657, Nov. 5, 1929, to Van Schaack Bros. Chemical Works, Inc.; *Chem. Abs.*, 1930, 24, 515) phenoxy phthalate (R. L. Kramer, British P. 306,911, 1928, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1929, 23, 5338), the phthalate of methyl salicylate (L. P. Kyrides, U. S. P. 1,979,559, Nov. 6, 1934, to Monsanto Chemicals Corp.; *Chem. Abs.*, 1935, 29, 177. British P. 421,420, 1933; *Brit. Chem. Abs. B*, 1935, 194),  $\beta$ -acetoxyethyl butyl phthalate (H. D. Young, U. S. P. 1,786,404, Dec. 28, 1930; *Chem. Abs.*, 1931, 25, 610) and di-( $\beta$ -methoxyethyl) phthalate (British P. 279,771, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1928, 22, 3044). On the preparation of  $\beta$ -methoxyethyl benzoate see R. C. Conn, A. R. Collett, and C. L. Lassell (*J.A.C.S.*, 1932, 54, 4371). R. H. Van Schaack, Jr., and R. Calvert make a plasticizer by acetylating di-( $\beta$ -hydroxyethyl) phthalate (U. S. P. 1,733,639, Oct. 29, 1929, to Van Schaack Bros. Chem. Works, Inc.; *Chem. Abs.*, 1930, 24, 379). They also recommend compounds like hydroxyethyl ethyl phthalate as high-boiling solvents and plasticizers (R. H. Van Schaack, Jr., and R. Calvert, U. S. P. 1,706,639, Mar. 26, 1929, to Van Schaack Bros. Chem. Works, Inc.; *Brit. Chem. Abs. B*, 1929, 636); also ethylene glycol phthalates or mixed esters of bis- $\beta$ -hydroxyethyl phthalate (R. H. Van Schaack, Jr., and R. Calvert, U. S. P. 1,922,646, May 8, 1933, to Van Schaack Bros. Chem. Works, Inc.; *Brit. Chem. Abs. B*, 1934, 546. J. M. Kessler and O. B. Helfrich form the phthalic esters of polyglycol monoalkyl ethers; for example, the phthalate of diethylene glycol monoethyl ether (U. S. P. 1,714,173, May 31, 1929, to Kessler Chemical Co.; *Chem. Abs.*, 1929, 23, 3583). The esters formed from saturated fatty acids and the ethylene glycol monoalkyl ethers also serve as plasticizers for cellulose esters (J. R. Buckley, U. S. P. 1,869,660, Aug. 2, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 5310). The esters of saturated acids, such as stearic, and ethers of diethylene glycol have been suggested (J. M. Kessler and O. B. Helfrich, U. S. P. 1,739,315, Dec. 10, 1929; *Chem. Abs.*, 1930, 24, 862).  $\beta$ -Butoxyethyl- $\beta$ -hydroxyethyl phthalate formed by esterifying glycol with phthalic acid and subsequent esterification with  $\beta$ -butoxyethanol, or vice versa, and compounds of this general structure have a high solvent power for plastics in general (R. B. Fraser, British P. 410,797, 1934, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1934, 28, 6443. French P. 746,467, 1933; *Chem. Abs.*, 1933, 27, 4539. See also H. Dreyfus, British P. 418,506, 1934; *Chem. Abs.*, 1935, 29, 2200.) This also applies to the esters of monoalkyl ethers of the polyglycols (E. F. Isard, U. S. P. 1,943,979, Jan. 16, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1934, 932). H. Dreyfus (British P. 420,221, 1933; *Brit. Chem. Abs. B*, 1935, 161) prepared cyclic monomeric esters by reacting ethylene glycol with phthalic anhydride in the presence of 0.5 per cent of orthophosphoric acid at 135°C. or by heating sodium  $\beta$ -chloroethyl phthalate at 150°C. and by treating  $\alpha$ -dicarbethoxyethylene and  $\beta\beta'$ -iminodiethyl phthalate. For alkoxyalkyl esters of long-chain dibasic acids see E. F. Isard, U. S. P. 1,991,891, Feb. 19, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 3176.

<sup>147</sup> T. P. Sager and E. G. Kennedy, Jr., *Physics*, 1931, 1, 353; *Chem. Abs.*, 1933, 26, 1908.

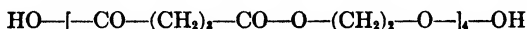
<sup>148</sup> A. D. Whipple, British P. 405,054, 1932, to Mantle Lamp Co. of America; *Brit. Chem. Abs. B*, 1934, 268. French P. 745,353, 1933; *Chem. Abs.*, 1933, 27, 4431.

<sup>149</sup> C. L. Gabriel and L. C. Swallen, U. S. P. 1,946,303, Feb. 6, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1934, 28, 2372.

lithium<sup>120</sup> and copper.<sup>121</sup> The presence of metallic compounds stabilizes the products against the destructive influences of light.

Ethylene glycol boils at a lower temperature (197°C.) than glycerol and when it is used to form a resin the reaction will be carried out at a lower temperature. The polyglycols or dihydroxy ethers, however, have fairly high boiling points. Of these, diethylene glycol has been used most widely. Gardner, Knauss and Van Heuckeroth<sup>122</sup> have used triethylene glycol. They heated equimolecular proportions of phthalic anhydride, triethylene glycol, and tartaric acid at 185-200°C. for 3 hours and obtained a pale amber viscous liquid resin, soluble in acetone, alcohol, and chloroform, insoluble in toluene, and compatible with nitrocellulose solutions. When heated for 15 to 18 hours this product becomes a dark amber plastic mass incompatible with nitrocellulose but compatible with cellulose acetate solutions. Exposure tests of lacquers containing equal parts of the dark resin and cellulose acetate gave fairly satisfactory results.

Glycol condenses with glutaric acid in the presence of zinc chloride at 135-140° to give a gummy acid ester.<sup>123</sup> The degree of polymerization of this ester is apparently less than in the succinic acid series and corresponds to the formula



1,3-Butylene glycol, when heated with phthalic anhydride to 160°C., gives a glassy product;<sup>124</sup> with maleic anhydride reaction also takes place.<sup>125</sup>

When the same glycol is heated to 100° with adipic acid, butyl alcohol and concentrated phosphoric acid, it yields a thick oil.<sup>126</sup>

Bradley<sup>127</sup> used glycols such as propane-1,2-diol, trimethylene glycol and 2,3-butyleneglycol. These react with phthalic anhydride to yield resins which are more soluble than those from glycerol. The resins from the first two glycols mentioned are partially soluble, and that from the third, completely soluble in toluene. A mixture containing one mol each of propane-1,2-diol and phthalic anhydride is heated in a partially closed vessel to 290°C. for approximately 2.5 hours. The product is a soft, straw-colored resin (acid number about 56). These resins improve gloss and adhesion when added to nitrocellulose lacquers.

Polyglycols are formed by heating ethylene glycol or by polymerizing ethylene oxide. The alkylene oxides themselves form various light-colored, viscous products when treated with polybasic acids. For example, water-soluble esters are produced by treating 1 mol of phthalic anhydride with 2 mols of ethylene oxide. The reaction is carried out in the presence of a small amount of sodium phthalate in an autoclave heated to 60-65°C. The product is a viscous liquid.<sup>128</sup> Succinic acid and ethylene oxide, heated in an autoclave at 80-90°C., also yield a viscous, water-soluble product.<sup>129</sup> Tetraethylene glycol,  $\text{HOCH}_2-(\text{CH}_2\text{OCH}_2)_3-\text{CH}_2\text{OH}$ ,

<sup>120</sup> A. D. Whipple, British P. 410,837, 1934, to the Mantle Lamp Co. of America; *Chem. Abs.*, 1934, 28, 6581.

<sup>121</sup> A. D. Whipple, British P. 411,154, 1934, to the Mantle Lamp Co. of America; *Chem. Abs.*, 1934, 28, 6583.

<sup>122</sup> H. A. Gardner, C. A. Knauss and A. W. Van Heuckeroth, *Ind. Eng. Chem.*, 1929, 21, 57.

<sup>123</sup> Y. Tsuzuki, *Bull. Chem. Soc. Japan*, 1933, 8, 313; 1935, 10, 17; *Brit. Chem. Abs. A*, 1934, 57; 1935, 474.

<sup>124</sup> German P. 545,780, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3687.

<sup>125</sup> K. Daimler and G. Balle, U. S. P. 1,934,671, Dec. 18, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 903.

<sup>126</sup> F. Moll, German P. 566,519, 1930, addition to 545,780, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2457.

<sup>127</sup> T. F. Bradley, U. S. P. 1,890,663, Dec. 13, 1932, to American Cyanamid Co.; *Chem. Abs.*, 1933, 27, 1774.

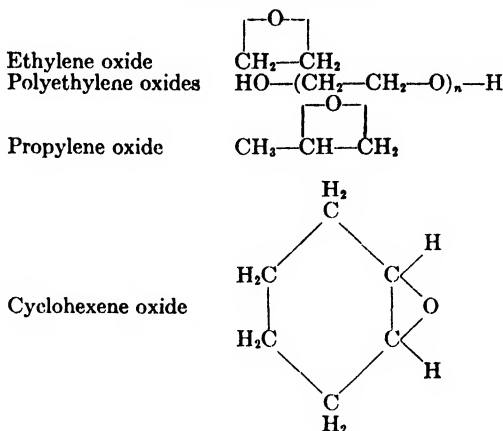
<sup>128</sup> F. Webel, U. S. P. 1,883,183, Oct. 18, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 731. German P. 543,617, 1927; *Chem. Abs.*, 1933, 26, 3364. British P. 302,041, 1927; *Chem. Abs.*, 1929, 23, 4329. Canadian P. 234,963, 1928; *Chem. Abs.*, 1929, 23, 849. French P. 647,513, 1928; *Chem. Abs.*, 1929, 23, 2448.

<sup>129</sup> F. Webel, German P. 544,388, 1928, addn. to 543,617, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 3313. Ethylene oxide may be used to neutralize the free fatty acids in vegetable oils by

can be prepared from ethylene oxide and triethylene glycol by a pressure reaction.<sup>100</sup>

Glycerol  $\beta$ -hydroxyethyl ether is formed by treating glycerol with ethylene oxide at an elevated temperature.<sup>101</sup> Heated with phthalic anhydride this com-

TABLE 45.—Oxides.



pound forms a soft mass which may be used as a plasticizer. With succinic acid the ether yields a viscous product which hardens on further heating to an insoluble, elastic resin. Sorbitol hydroxyethyl ethers are obtained in the same way and can be used in aqueous solution instead of glycerol to soften water-soluble plastics. The ethers have been suggested as softeners for casein, nitrocellulose or rubber.<sup>102</sup> When these hydroxyethyl ethers are treated with polybasic acids, heavy, balsam-like liquids are produced.

Pentaerythritol can also be treated with ethylene oxide in the presence of boric acid. The product is a viscous liquid insoluble in water, acetone and alcohol but soluble in many organic solvents.<sup>103</sup> The reaction of other alkylene oxides (propylene oxide, tetrahydrobenzene oxide) with pentaerythritol results in the production of etherified alcohols of high boiling point and of a viscous nature which find use in paper making, in explosives, in textile processes, as lubricants and as solvents or separating agents. These esterified alcohols when acetylated with either monobasic acids or polybasic acids give plasticizing substances and camphor substitutes. The nitric acid esters may be used in films, plastics, lacquers and explosives.<sup>104</sup>

Ethylene oxide may also be used to neutralize the acidity of resins. For example, a hard, fusible resin of acid number 130, obtained by heating 444 parts phthalic anhydride and 184 parts glycerol, was treated in an autoclave with about 140 parts ethylene oxide for six hours at 150°C. The product was a light-colored, clear, viscous balsam whose acid number was zero.<sup>105</sup>

heating the solution under pressure. See British P. 312,523, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 983.

<sup>100</sup> See T. P. Sager, page 891, for preparing a ground-joint lubricant by reacting triethylene glycol with citric acid.

<sup>101</sup> O. Loehr, German P. 510,422, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 964. British P. 313,892, 1927; *Chem. Abs.*, 1930, 24, 1119. French P. 652,383, 1928; *Chem. Abs.*, 1929, 23, 3476.

<sup>102</sup> O. Schmidt and E. Meyer, German P. 538,687, 1927, and addn. 540,723, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2287. British P. 317,770, 1928; *Chem. Abs.*, 1930, 24, 2141.

<sup>103</sup> S. Malowan, *Plastic Products*, 1934, 10, 147. See also, *Farbe und Lack*, 1934, 30; *Brit. Chem. Abs.* B, 1934, 288.

<sup>104</sup> O. Schmidt and E. Meyer, U. S. P. 1,922,459, Aug. 13, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5082. See U. S. P. 1,959,930, May 22, 1934; *Chem. Abs.*, 1934, 28, 4430 and German P. 598,596, 1934; *Chem. Abs.*, 1934, 28, 5632.

<sup>105</sup> O. Schmidt and E. Meyer, U. S. P. 1,845,193, Feb. 16, 1933, to I. G. Farbenind. A.-G.; *Chem.*

Ethylene oxide reacts with cellulose to form hydroxyethyl ethers which, when treated with polybasic acids, form esters having a resinous character. They may be molded or used in lacquers.<sup>166</sup>

Ether-alcohols, other than the hydroxyalkyl ethers, also yield resins. Lawson<sup>167</sup> heated monoethylin (glycerol monoethyl ether) with phthalic anhydride and obtained a product which can be used with nitrocellulose or ethyl cellulose in lacquers. Hahn<sup>168</sup> formulated a cellulose acetate lacquer consisting of 12 parts of monoethylin phthalate resin, 12 parts cellulose acetate and 6 parts of a softener (diethyl or dibutyl phthalate) dissolved in 79 parts by weight of solvent. Another resin from monoethylin is made by heating 1 mol of glycerol ether with 2 mols of benzoylbenzoic acid at 175-250°C. for 3-14 hours.<sup>169</sup> Nitrocellulose plasticizers can be prepared from the acid phthalic ester of monoethylin by esterifying the free carboxyl groups with a monohydric alcohol. Butyl monoethylin phthalate is a substance of this type.<sup>170</sup>

Scheiber<sup>171</sup> also used polyhydric alcohols which had been partly etherified by a monohydric alcohol. These are condensed with polybasic acids by heating at about 200°C. For example, he made a resin by heating phthalic anhydride and glycerol monomethyl ether.

Hoover<sup>172</sup> used glycerol ethers such as the monophenyl or monotetrahydrofurfuryl derivatives. A mixture of 420 parts of  $\alpha$ -glyceryl phenyl ether (1-phenoxy-2,3-propanediol,  $\text{CH}_2\text{OHCHOHCH}_2\text{OC}_6\text{H}_5$ ) and 370 parts of phthalic anhydride are brought to 220-225°C. during the course of 2 to 3 hours and heating is continued within this range of temperature until a test sample has an acid number of 10 or less. The finished product is a hard clear resin having a brownish-red color. It is soluble in organic esters and aromatic hydrocarbons and in the mixtures of esters, alcohols and hydrocarbons ordinarily used in lacquer compositions. It is compatible with nitrocellulose in all proportions. Another resin is made by heating 112 parts of the tetrahydrofurfuryl ether of glycerol ( $\text{C}_6\text{H}_5\text{OCH}_2\text{CHOHCH}_2\text{OH}$ ) and 96 parts of phthalic anhydride. The finished resin has an acid number of approximately 10 and is a soft, clear mass, dark brown in color. It is soluble in acetone, or in a mixture of alcohol and benzene. The resin from phenol glycerol ether and phthalic anhydride can be incorporated with rubber and the mixture vulcanized to yield a rubber mass of increased resistance to chemical and electrical effects.<sup>173</sup>

#### PENTAERYTHRITOL

By the condensation of formaldehyde and acetaldehyde in the presence of calcium hydroxide, pentaerythritol, a tetrahydric alcohol, is obtained.<sup>174</sup>

*Abs.*, 1932, 26, 2334. German P. 561,626, 1927. French P. 662,603, 1928, to I. G. Farbenind. A. G.; *Chem. Abs.*, 1930, 24, 516. British P. 328,190, 1928; *Brit. Chem. Abs. B*, 1930, 677.

<sup>166</sup> French P. 705,816, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 303.

<sup>167</sup> W. E. Lawson, U. S. P. 1,967,955, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 6002. British P. 316,325, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 24, 1784. Canadian P. 324,955, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 5439.

<sup>168</sup> F. C. Hahn, U. S. P. 1,812,335, June 30, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 5049. Canadian P. 312,569, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1931, 25, 4422. British P. 316,328, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 1754.

<sup>169</sup> F. C. Hahn, U. S. P. 1,909,195, May 16, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 3337. British P. 316,322, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 1764. Canadian P. 323,650, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 3945.

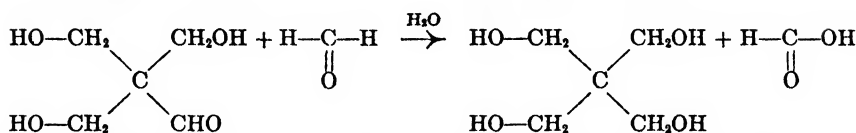
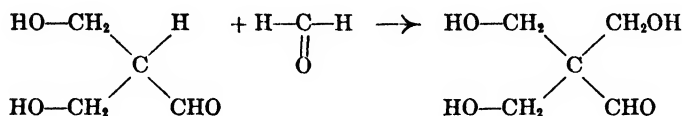
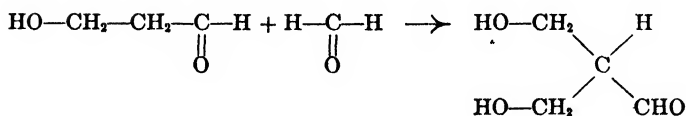
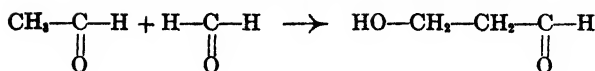
<sup>170</sup> W. E. Lawson, U. S. P. 1,909,196 and 1,909,197, May 16, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 3721. British P. 316,324, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 1650. Canadian P. 310,133, 1931, to Canadian Industries, Ltd.

<sup>171</sup> J. Scheiber, German P. 637,637, 1928; *Chem. Abs.*, 1932, 26, 1461.

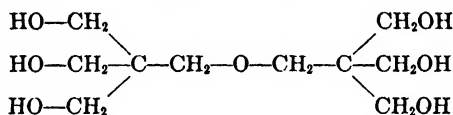
<sup>172</sup> K. H. Hoover, U. S. P. 1,855,049, Apr. 12, 1932, to Association of American Soap and Glycerine Producers, Inc.; *Chem. Abs.*, 1932, 26, 3399.

<sup>173</sup> Swiss P. 165,713, 1934, to J. R. Geigy A.-G.; *Chem. Abs.*, 1934, 28, 2946.

<sup>174</sup> C. E. Burke, U. S. P. 1,716,110, June 4, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*,



There is also formed simultaneously a small amount of dipentaerythritol,<sup>175</sup>



which occurs in the commercial material. Von Herz<sup>176</sup> heated pentaerythritol and phthalic anhydride at 140°C. until the anhydride ceased to sublime and obtained a soluble resin which when heated at higher temperatures became insoluble and infusible.<sup>177</sup> Pentaerythritol, condensed with succinic acid, a mixture of succinic acid and phthalic anhydride, or with glycerol and maleic acid, also gives moldable resins.<sup>178</sup> Bruson<sup>179</sup> made a nitrocellulose plasticizer by the reaction of pentaerythritol and 9,10-dihydroxystearic acid. Burke<sup>180</sup> used the mono-, di- or triethyl ethers of pentaerythritol for the same purpose. These ethers are formed by the action of ethyl chloride on pentaerythritol in the presence of sodium carbonate.

Clarke<sup>181</sup> has prepared pentaerythritol tetra-acetate by reacting acetic acid and pentaerythritol and distilling off the water. Linseed oil acids may also be esterified with pentaerythritol by using 0.05 per cent of lead monoxide.<sup>182</sup> Pentaerythritol,

1929, 23, 3717. See also J. Meisner, French P. 702,416, 1930; *Chem. Abs.*, 1931, 25, 4286. German P. 538,916, 1929; *Chem. Abs.*, 1932, 26, 2202. E. Naujoks, German P. 596,509, 1934, to Deutsche Gold- & Silber-Scheidanstalt vorm. Roesler; *Chem. Abs.*, 1934, 28, 5081. British P. 404,975, 1932; *Brit. Chem. Abs.* B, 1934, 266. French P. 744,397, 1933; *Chem. Abs.*, 1933, 27, 3953. T. Sakai, Japanese P. 94,210, 1932, to the War Minister; *Chem. Abs.*, 1933, 27, 2697. For use of catalysts other than calcium hydroxide, see A. Corbellini and A. Langini, *Giorn. chim. ind. applicata*, 1933, 15, 53; *Chem. Abs.*, 1933, 27, 4526 and H. Molinari, *Giorn. chim. ind. applicata*, 1933, 15, 325; *Chem. Abs.*, 1934, 28, 104. For determination of pentaerythritol, see M. Y. Kraft, *J. Chem. Ind., Russia*, 1931, 8, 507; *Brit. Chem. Abs.* A, 1932, 72 and H. A. Aaronson, U. S. P. 1,678,623, July 24, 1928; *Chem. Abs.*, 1928, 22, 3418.

<sup>175</sup> W. Friederich and W. Brün, *Ber.*, 1930, 63, 2681; *Chem. Abs.*, 1931, 25, 1486. According to L. Ebert (*Ber.*, 1931, 64, 114; *Brit. Chem. Abs.* A, 1931, 334) the most efficient method for the purification of pentaerythritol is by sublimation in a high vacuum at about 130°.

<sup>176</sup> E. von Herz, German P. 501,955, 1927. *British P.* 301,429, 1928; *Brit. Chem. Abs.* B, 1930, 520. French P. 671,208, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1997.

<sup>177</sup> C. E. Burke and H. H. Hopkins, U. S. P. 1,667,189, Apr. 24, 1928, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1928, 22, 2071. *British P.* 289,794, 1927, to Nobel Industries, Ltd.; *Chem. Abs.*, 1929, 23, 1002. Canadian P. 383,398, 1930, to Canadian Industries, Ltd. See Chapter 44.

<sup>178</sup> German P. 554,857, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 6163.

<sup>179</sup> H. A. Bruson, U. S. P. 1,835,203, Dec. 8, 1931, to Röhnm & Haas Co.; *Chem. Abs.*, 1932, 26, 1120.

<sup>180</sup> C. E. Burke, U. S. P. 1,774,500, Sept. 2, 1930, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1931, 631.

<sup>181</sup> H. T. Clarke, U. S. P. 1,532,653, May 4, 1926; *Chem. Abs.*, 1926, 20, 1996.

<sup>182</sup> *British P.* 406,536, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1934, 334.

on heating with dicarboxyethers or with thio-ethers and their anhydrides (diglycolic acid, carboxymethyl ether of salicylic acid, methyl diglycolic acid and thio-diglycolic acid, sulphidodiacetic acid), yield resins which form substitutes for glass, horn or shellac.<sup>188</sup>

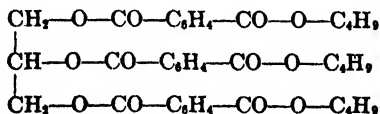
#### MIXTURES OF POLYHYDRIC ALCOHOLS

Hill and Walker<sup>184</sup> used a mixture of ethylene glycol and glycerol to make resins of improved solubility and low acid number. Ordinary phthalic glyceride resins are very sparingly soluble in ester solvents, have a high acid number and if heated too long they change to an infusible, insoluble form. In order to make a more soluble resin, the glycerol is partly replaced by glycol. The incorporation of a dihydric alcohol allows heating to a high temperature without causing insolubility. A transparent, brittle resin made from 370 parts phthalic anhydride, 250 parts glycerol and 50 parts ethylene glycol, after heating 5 hours at about 200°C. was still soluble and had an acid number of only 2.7. These resins may be made in one step, or phthalic glycol resin and phthalic glyceride may be fused together. Kienle<sup>185</sup> also described polybasic acid resins from glycerol and glycol, diethylene glycol or propylene glycol.

#### MONOHYDRIC ALCOHOLS

Part of the polyhydric alcohol used in the resin reaction with polybasic acids may be replaced by monohydric alcohols (ethyl, amyl, butyl, allyl, diacetone alcohols or borneol). The products thus obtained are soft, depending upon the amount of monohydric alcohol employed and are useful for coating wires and sheet metal because of their high flexibility and water-resistivity. A clear and transparent resin can be made up as follows: To the reaction product of 285 parts of phthalic anhydride and 40 parts of butyl alcohol, which have been heated for 1.5 hours at 160°C., 100 parts of glycerol are added and the mass re-heated to 200-220°C.<sup>186</sup> Hill and Walker<sup>187</sup> made a phthalic anhydride-glycerol-butyl alcohol resin as follows: To a mixture of 18.5 parts of butyl alcohol and 74 parts of phthalic anhydride heated under an air condenser to about 200°C. for an hour, 23 parts of glycerol are added and the temperature held at 185-195°C. for 4 hours. On cooling, the product is a tough resin soluble in acetone and having an acid number of 48. If the butyl alcohol is replaced by glycerol, the resin gels in about 3 hours and the acid number just before gelation is close to 100. Cyclohexanol may be used in the same way as butanol.

Arsem<sup>188</sup> sought to prepare ester groupings containing no free carboxyl groups or hydroxyl groups. The product of butyl alcohol, phthalic anhydride and glycerol would be represented as follows:



<sup>188</sup> British P. 337,722, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 624.

<sup>184</sup> R. Hill and E. E. Walker, British P. 305,965, 1927, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.* B, 1929, 333. French P. 663,540, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 740.

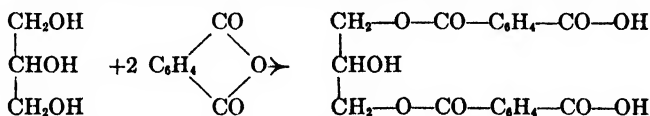
<sup>185</sup> R. H. Kienle, British P. 317,767, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1930, 24, 3317. French P. 690,449, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1930, 24, 3914.

<sup>186</sup> R. H. Kienle, U. S. P. 1,921,756, Aug. 3, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 5203. British P. 399,424, 1933, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 23, 3360. French P. 663,518, 1928, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1930, 24, 516. German P. 534,314, 1928, to Allgemeine Elektrizitäts Ges.; *Chem. Abs.*, 1932, 26, 861.

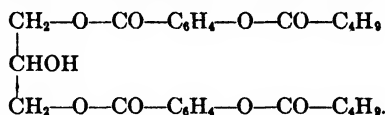
<sup>187</sup> R. Hill and E. E. Walker, British P. 305,965, 1927, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.* B, 1929, 333. French P. 663,540, 1928; *Chem. Abs.*, 1930, 24, 740.

<sup>188</sup> W. C. Arsem, U. S. P. 1,935,791, Dec. 12, 1933; *Chem. Abs.*, 1934, 28, 1533. See also German P. 609,249, 1936, to Dageb A.-G.; *Chem. Abs.*, 1936, 29, 3072.

By first heating two mols (296 grams) of phthalic anhydride and one mol (92 grams) of glycerol at 150-200°C., glyceryl phthalic acid is produced:



To the latter is added a large excess of butyl alcohol, benzene and 10-20 g. of sulphuric acid. The butyl alcohol is distilled off, water being removed from the reaction as a constant-boiling mixture with benzene to yield the compound:



More alcohol and benzene are added and distillation carried out at reduced pressure to remove traces of water. By initially using 3 mols of phthalic anhydride to one mol of glycerol and esterifying similarly with butanol, the hydroxyl-free ester is obtained. Swallen and Ireys<sup>190</sup> have improved the method of Arsem by using a petroleum hydrocarbon to remove undesirable by-products. One mol (92 g.) of glycerol and 1.5 mols (222 g.) of phthalic anhydride are fused at 130-135°C. and the mass is then heated at 160°C. for 10 minutes. To this product are added 300 g. of n-butyl alcohol together with 22 g. of hydrochloric acid (sp. gr. 1.2). The resulting mixture is heated quickly to 110° C. and distilled first through a fractionating column and then *in vacuo*. The material is subsequently heated at 175-190°C. for 10-30 hours and then agitated with a petroleum hydrocarbon (b.p. 95-160°C.) at 90°C. for a few hours. The extraction with the hydrocarbon is continued until the resin is free of dibutyl phthalate. The residual hydrocarbon is removed along with by-products by heating to 120°C. under reduced pressure.<sup>190</sup>

Cetyl alcohol ( $\text{C}_{18}\text{H}_{37}\text{OH}$ ), on reacting with phthalic anhydride, yields a waxy ester; cetyl alcohol, phthalic anhydride and glycerol, a viscous balsam-like resin. These cetyl alcohol esters may be blended with nitrocellulose to produce films of a clear transparent character.<sup>191</sup> The resin made from 121 parts of cetyl alcohol, 148 parts of phthalic anhydride and 47 parts of glycerol by heating to 250°C. for 15 minutes and subsequently at 270°C. for 25 minutes is a viscous balsam, melting at 12°C. and of acid number 40. The products are miscible with butyl acetate, toluene and naphtha but not with denatured alcohol. Brubaker<sup>191a</sup> used a mixture of phthalic anhydride, glycerol and lauryl alcohol or the alcohols obtained by catalytic hydrogenation of fatty oils.

Terpene derivatives can also be included in the resin. Adams<sup>192</sup> heated a mixture of phthalic anhydride and terpene hydrate at 200°C. until a clear liquid was obtained. Glycerol was then added and the heating continued until a sample of the resin hardened on cooling. Borneol, camphoric anhydride and gutta-percha can be used. The resins obtained in this way have good water-resistance.

<sup>190</sup> L. C. Swallen and K. M. Ireys, U. S. P. 1,993,700, Mar. 5, 1935, to Commercial Solvents Corp.; *Chem. Abs.*, 1935, 29, 2623.

<sup>190</sup> For the use of the lauryl alcohol ester of phthalic acid as a plasticiser in cellulose varnishes see British P. 367,534, 1932, to Deutsche Hydrierwerke A.-G.; *Brit. Chem. Abs. B*, 1933, 317.

<sup>191</sup> T. F. Bradley, U. S. P. 1,951,593, March 20, 1934, and 1,953,583, Apr. 3, 1934, to American Cyanamid Co.; *Chem. Abs.*, 1934, 28, 3416, 3902.

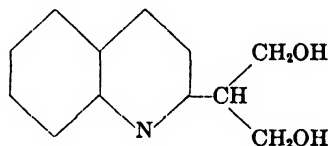
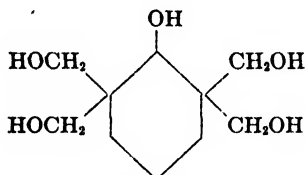
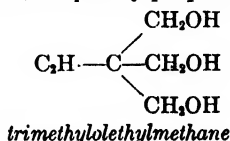
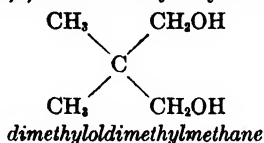
<sup>191a</sup> M. M. Brubaker, British P. 422,845, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1935, 278.

<sup>192</sup> L. V. Adams, U. S. P. 1,904,595, Apr. 18, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 3629. British P. 244,405, 1929, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1931, 596. Canadian P. 321,620, 1932, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1932, 26, 3392. French P. 653,772, 1929, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1930, 24, 5172. German P. 557,628, 1929, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1933, 27, 616.

## MISCELLANEOUS ALCOHOLS

Alcoholamines (mono-, di- or triethanolamine) form resins when heated with phthalic anhydride. The products are used as softening agents or as accelerators for vulcanization.<sup>196</sup> Weisberg and Greenwald<sup>194</sup> extended this reaction to include a combination of triethanolamine, phthalic anhydride and oleic acid. The amine and acid are first allowed to react at 150°C. whereupon the oleic acid is added. Substitution of citric acid in place of the oleic leads to considerable foaming.<sup>195</sup>

Burns<sup>199</sup> has used hexahydroxycyclohexane or its mono- or dimethyl ether (quebrachitol) as a polyhydric alcohol with phthalic anhydride in the preparation of resins. Other alcohols include dimethyloldimethylmethane, trimethylolethylmethane, 2,2,6,6-tetramethylolcyclohexanol and  $\beta$ -2-quinolylpropane- $\alpha,\gamma$ -diol.<sup>197</sup>



Cellulose itself reacts with phthalic anhydride in the presence of pyridine at 60°C. to form a white mass.<sup>198</sup> Cellulose phthalate can also be prepared by treating undissolved cellulose (either modified or partially etherified or esterified) with phthalic anhydride along with a tertiary organic base until a dope is formed. Under these conditions one of the carboxyl groups of the phthalic anhydride is esterified with the cellulose whereas the other combines with the organic base. Treatment with acid removes the base. When the reaction is carried out below 95°C. in the presence of benzene or ethylene dichloride and the compound precipitated, a product is formed which is soluble in water, rendered basic with pyridine, or in pyridine solutions of benzene or of tetrachloroethane.<sup>199</sup>

Cellulose can be similarly treated with succinic, glutaric, diglycolic, dilactic, dihydracrylic, thiodiglycolic, thiolactic acids and the like.<sup>200</sup> These acids may be neutralized with ammonia, alkylolamines or treated with heavy-metal salts.<sup>201</sup> Cellulose triethanolamine phthalate is used in making anti-halation coatings for backing photographic films.<sup>202</sup>

<sup>196</sup> British P. 376,929, 1931, and addn. 378,596, to Chem. Fabr. Dr. K. Albert G.m.b.H.; *Brit. Chem. Abs. B*, 1932, 948, 998. French P. 121,453, 1931; *Chem. Abs.*, 1932, 26, 4192. German P. 596,114, 1934; *Chem. Abs.*, 1934, 28, 4616.

<sup>194</sup> L. Weisberg and W. F. Greenwald, U. S. P. 1,918,222, July 11, 1933, to Weisberg & Greenwald, Inc.; *Chem. Abs.*, 1933, 27, 4701.

<sup>195</sup> The mixtures of triethanolamine with acids (phthalic, benzoic, salicylic or naphthalene sulphonic) may be incorporated into soap. See French P. 765,836, 1934, to Ormul Products, Ltd.; *Chem. Abs.*, 1934, 28, 7050.

<sup>199</sup> R. Burns, British P. 408,597, 1932, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1934, 547. <sup>197</sup> British P. 419,604, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1935, 112; *Chem. Abs.*, 1935, 29, 2628.

<sup>198</sup> Swiss P. 142,173, 1923, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1931, 25, 2238.

<sup>200</sup> British P. 410,118, 1934, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 6307.

<sup>201</sup> British P. 410,125, 1934, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 6307.

<sup>202</sup> British P. 410,126, 1934, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 6307.

<sup>197</sup> C. R. Fordyce, U. S. P. 1,969,741, Aug. 14, 1934, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 6307, 6308. British P. 410,236, 1934, to Kodak, Ltd.; *Chem. Abs.*, 1934, 28, 6076. See French P. 761,951, 1934, to Kodak Pathé; *Chem. Abs.*, 1934, 28, 4453.



## Chapter 43

### Modified Alkyd Resins

#### I. Use of Non-Drying Oils and Acids Effect of Natural Resins

The modification of alkyd resins with monobasic acids imparts increased solubility to the resin. Lower aliphatic acids (acetic, butyric) have a pronounced softening action. Acids from non-drying oils (stearic, palmitic, oleic, ricinoleic) lead to the formation of products of greater flexibility.<sup>1</sup> As a rule the free acids are used instead of the oils themselves since, with the exception of castor oil, it is difficult to incorporate the glyceride oils in an alkyd resin unless indirect methods are used. Other monobasic acids used with alkyd resins include natural resins (rosin, copal) which increase solubility and brittleness. The main use for all these modified resins is in coating compositions, particularly nitrocellulose lacquers.<sup>2</sup>

#### USE OF ACIDS FROM NON-DRYING OILS

Arsem<sup>3</sup> described the preparation of glycerol phthalate resins modified by oleic acid. Such a product is obtained when 92 parts of glycerol are heated with 148 parts of phthalic anhydride at 200-210°C. until evolution of water vapor ceases, after which a mixture of 141 parts of oleic acid and 37 parts of phthalic anhydride is added. On further heating at 215-230°C. for 1.5 hours a deep red liquid is obtained which congeals at room temperature. It is soluble in organic hydrocarbon-solvents, and may be hardened by prolonged heating (20-30 hours) at 160°C., but retains its flexibility. Increase in the proportion of oleic acid improves the elasticity. The hardened resin, which is transparent in thin layers, is insoluble, unattacked by weak acids or by chlorine, and little affected by long heating at 150°C. The liquid resin or its solutions, or solutions of a product partially hardened at 160°C., may be used for impregnating fabrics, wood or paper, or as a direct insulating coating for metal surfaces.

One application of the resin made by reaction of glycerol with phthalic anhydride and oleic acid is to coat electrodes which come in contact with litharge. The latter has been found to affect linseed oil but does not destroy the alkyd coating. The resin is applied in acetone solution and when the coating is baked a surface is obtained which exhibits a greater degree of resistance to water than is shown by shellac.

The addition of sulphur<sup>4</sup> to the oleic acid-modified alkyd yields rubber-like masses insoluble in solvents, although somewhat attacked by benzene and by xylene. These are infusible, but char like rubber on heating. By use of molecular

<sup>1</sup> The monobasic acids from drying oils also impart increased solubility and flexibility and at the same time cause the resin to be more susceptible to heat-hardening. (See Chapter 44.) In contrast, the non-oxidizable acids of non-drying oils make the resin less sensitive to heat-hardening, the effect depending upon the proportion of monobasic acid used.

<sup>2</sup> See Chapter 47.

<sup>3</sup> W. C. Arsem, U. S. P. 1,098,777, June 2, 1916, to General Electric Co.; *Chem. Abs.*, 1914, 8, 2818.

<sup>4</sup> W. C. Arsem, U. S. P. 1,083,106, Dec. 22, 1913, to General Elec. Co.; *Chem. Abs.*, 1914, 8, 830.

proportions of glycerol and phthalic acid, with subsequent addition of 1 mol of oleic acid at 210-215°C., a viscous liquid is obtained to which 10-20 per cent of sulphur is added. Up to 19 per cent of castor oil may also be incorporated. The product may be used for stoppers, washers and molded material in place of rubber.

By the use of lactic acid or chloroacetic acid with glycerol-phthalic anhydride, resins of low flow-point are obtained; thus the resin produced by one-quarter mol of chloroacetic acid and one and three-eighth mols of phthalic anhydride per mol of glycerol has a flow point of 88°C., is hard and brittle and is rendered infusible by heating at 160°C. for 8 hours.<sup>5</sup> Butyric acid<sup>6</sup> combined with glycerol phthalate yields a very soft rubber-like product, which may be dissolved in acetone and used to impregnate wood, cloth and paper, the resin being rendered insoluble and infusible by heating 2 or 3 hours at 100-120°C. while still retaining flexibility. Such a resin may be procured by heating 22 parts of glycerol phthalate (from 2 parts by weight of phthalic anhydride and 1 part of glycerol) with 10 parts of butyric or isobutyric acid in glycerol for 8-24 hours. The temperature is finally raised to 300°C.

Arsem<sup>7</sup> heated glycerol phthalate with stearic acid and obtained a soft, paraffin-like substance which was soluble in heavy hydrocarbons and had good insulative properties. Alkyd resins modified with stearic or other fatty acids are not homogeneous and contain ingredients which confer solvent retentiveness on their solutions. Quick-drying resins may be formed, however, by treating the mass with solvents<sup>8</sup> (gasoline or 95 per cent alcohol) which dissolve out the slow-drying constituents. The residual resins are then quicker-drying, and harden more rapidly under heat treatment. Addition of the acids derived from coconut oil to the stearic acid-modified alkyd also improves the drying qualities without impairing the fastness to light.<sup>9</sup> For example, a resin was prepared from 100 parts of glycerol, 160 parts of phthalic anhydride, 45 parts of stearic acid and 45 parts of the distilled acids of coconut oil by heating at 200-290°C. in an inert atmosphere.

Cottonseed oil acid-modified glycerol phthalate resins are soluble in acetone and may be incorporated with nitrocellulose in any proportion to form lacquer coatings.<sup>10</sup> Soluble resins for coating compositions are also made by treating a glycerol phthalate-cottonseed oil acid resin with 1-2 per cent of its weight of sulphur monochloride.<sup>11</sup> The product from 80 parts of phthalic anhydride, 50 parts of glycerol and 45 parts of the distilled fatty acids from cottonseed oil, brought to acid number 25 by heating to 230°C., is dissolved in toluene-monochlorobenzene, or benzene-ethyl acetate mixture, and treated with 1 per cent of sulphur monochloride. The free acids are neutralized after 2 hours with magnesium oxide giving a solution which may be incorporated with cellulose esters, plasticizers and pigments. By heating together glycerol, phthalic anhydride, oleic acid and ammonium acid sulphate to 170-240°C., a vigorous reaction sets in and a dark resin is produced which is soft, transparent and adhesive. The composition is soluble in benzene and toluene and blends well with nitrocellulose in a solvent consisting of butyl acetate and toluene.<sup>12</sup>

Modified alkyd resins, such as that derived from 80 parts of phthalic anhydride,

<sup>5</sup> W. C. Arsem, U. S. P. 1,093,776, June 2, 1914, to General Elec. Co.; *Chem. Abs.*, 1914, 8, 2816.

<sup>6</sup> L. H. Friedburg, U. S. P. 1,119,592, Dec. 1, 1914, to General Elec. Co.; *Chem. Abs.*, 1915, 9, 179.

<sup>7</sup> W. C. Arsem, U. S. P. 1,093,776, June 2, 1914, to General Elec. Co.; *Chem. Abs.*, 1914, 8, 2816.

<sup>8</sup> Carleton Ellis, U. S. P. 1,392,423, Dec. 27, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 2321.

<sup>9</sup> British P. 356,141, 1930, to Amer. Cyanamid Co.; *Brit. Chem. Abs. B*, 1931, 1019. French P. 685,424, 1930; *Chem. Abs.*, 1931, 25, 2368.

<sup>10</sup> Carleton Ellis, U. S. P. 1,923,714, Aug. 22, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 5560.

<sup>11</sup> Carleton Ellis, U. S. P. 1,811,115, June 23, 1931; *Chem. Abs.*, 1931, 25, 8049.

<sup>12</sup> Carleton Ellis, U. S. P. 1,970,518, Aug. 14, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 6330.

50 parts of glycerol and 45 parts of cottonseed oil acids<sup>12</sup> thinned with a hydrocarbon solvent, have been used with wood flour and pigments, for a wood filler or coating composition which bonds well with superposed lacquer.

In the manufacture of water-resistant abrasants (emery and whetstone), a binding composition is made up with a resin resulting from condensation of glycerol, glycol and a fatty acid of at least ten carbons (lauric, palmitic, and stearic) and a polybasic acid (phthalic, maleic or succinic).<sup>14</sup>

When the oleic acid-modified glycol-phthalate resin is sulphonated with chloro-sulphonic acid, water-soluble resinous products result which act as resolving agents for water-in-oil emulsions.<sup>15</sup>

By employing a succinic acid-benzoic acid-glycerol mixture<sup>16</sup> light-colored resins of great toughness are formed which blend well with cellulose esters. Such a product is obtained from 61 parts of benzoic acid, 59 parts of succinic acid and 46.5 parts of glycerol, heated slowly to 290°C. and chilled rapidly. The resin may be used with, for example, an equal weight of cellulose acetate in a mutual solvent, such as a mixture of 10 per cent acetone, 30 per cent ethyl oxybutyrate and 60 per cent ethylene dichloride. The product from succinic acid and dihydroxy-diethyl ether (diethylene glycol) has especially high blending powers with nitrocellulose.

The ester prepared from benzoic acid and glycerol,<sup>17</sup> though soluble in ethyl, butyl and amyl acetates, is nevertheless quite soft. Addition of phthalic anhydride improves the hardness and at the same time does not limit the solubility in ester solvents provided that not too much phthalic anhydride is used. Glycerol benzoate-phthalate is of a pale color when prepared by heating in a vacuum and is soluble in ester solvents, softens easily and mixes well with nitrocellulose to form a lacquer. Ethylene glycol, propylene glycol and chlorohydrins may replace the glycerol with no appreciable change in properties.

#### USE OF FATTY OILS

Howell<sup>18</sup> found that both the toughness and the flexibility of alkyd resins were improved by the incorporation of castor oil. He first partially esterified 184 parts of glycerol with 296 parts of phthalic anhydride by heating for about 1 hour at 180°C.; 320 parts of castor oil were then added. At first the oil formed a distinct layer but on continued heating at 220°C. solution took place and a homogeneous liquid resulted. At this stage the resin was soluble in alcoholic benzene (1-3) but quite insoluble in benzene itself. By further heating to 280°C. a violent gas evolution occurred and a vesiculated infusible product was obtained.

This resin may be further modified by the addition of oleic acid<sup>19</sup> in accordance with the following procedure: 92 parts of glycerol and 148 parts of phthalic anhydride are heated to 200°C. and 70.5 parts of oleic acid, 70.5 parts of castor oil and 37 parts of phthalic anhydride added. The flexible condensation product is soluble in hydrocarbons (benzene, naphtha, turpentine, coal-tar oil) and forms a varnish for impregnating paper. When mixed with a mineral filler the resin may be applied directly to metallic surfaces. The hardened resin is resistant to dilute acid or alkali but is attacked by more concentrated solutions.

<sup>12</sup> P. S. Kennedy, U. S. P. 1,903,768, Apr. 18, 1933, to Murphy Varnish Co.; *Chem. Abs.*, 1933, 27, 3350.

<sup>14</sup> British P. 376,121, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3310.

<sup>15</sup> T. B. Wayne, U. S. P. 1,919,871, July 23, 1933; *Brit. Chem. Abs.* B, 1934, 440. Patent also mentions other resins (anisole-formaldehyde-oleic acid) which may be solubilized by sulphonation.

<sup>16</sup> Carleton Ellis, U. S. P. 1,886,242, Nov. 1, 1932, to Ellis-Foster Co.; *Brit. Chem. Abs.* B, 1933, 719.

<sup>17</sup> T. F. Bradley, U. S. P. 1,956,559, May 1, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 4255.

<sup>18</sup> K. B. Howell, U. S. P. 1,098,728, June 2, 1914, to General Elec. Co.

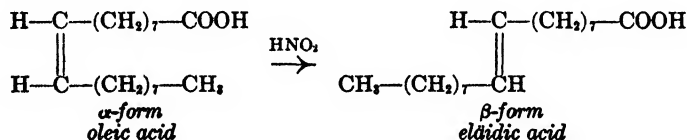
<sup>19</sup> E. S. Dawson, U. S. P. 1,141,944, June 3, 1915, to General Elec. Co.; *Chem. Abs.*, 1915, 9, 1973.

The castor oil-modified alkyds are compatible with nitrocellulose<sup>20</sup> and in admixture with the latter form lacquers for coating artificial leather.<sup>21</sup> Castor oil resins can be bleached by heating them with a small amount of phosphoric or boric acid and exposing to light for several days.<sup>22</sup>

Elastic products, approximating the properties of natural Hevea rubber are made, according to Bruson,<sup>23</sup> by heating castor oil with an aliphatic dibasic acid (adipic, pimelic, suberic, azelaic, or sebacic) and a polyhydric alcohol. Drying oils (linseed oil) may also be incorporated. In this way, by heating 55 parts of glycerol, 181.8 parts of sebacic acid and 189.6 parts of castor oil for 10 hours at 190–200°C., a rubbery mass is produced, soluble in butyl alcohol and toluene. Longer heating insolubilizes it, but the material is capable of being rendered soluble again by mastication in a rubber mill. The products may be used as plasticizers for cellulose nitrate lacquers and as bonding materials for rubber, wood flour and clay pigments. In place of castor oil, its hydrolytic product, ricinoleic acid, may be substituted.<sup>24</sup>

Resins can also be prepared from oxidized fats. When air or other gas containing oxygen is forced through the glycerol esters of fatty acids (glycerol-oleic ester), a liquid of high viscosity is obtained, provided the oxidation has not been allowed to proceed to the gelatinizing stage. Condensation with maleic anhydride then yields a resin with an acid number of 30–40.<sup>24</sup>

An interesting development arises from the observation that geometrical isomerism has a distinct bearing on the characteristics of the resin. The  $\beta$ -form of the acid yields products which are harder and have greater resistance to aging and oxidation than those from the  $\alpha$ -acid.<sup>25</sup> The  $\alpha$ - and  $\beta$ -forms are related as "cis" and "trans" isomers, the low-melting  $\alpha$ -form being converted to the higher-melting  $\beta$ -form by nitrous acid:



Natural fats (olive oil and castor oil) of iodine number more than 70 are converted by shaking with freshly prepared nitrous acid solution to give the  $\beta$ -form, and the resulting eläidin, or ricineläidin, is reacted with glycerol and phthalic anhydride. The  $\beta$ -form of olive oil (37.7 parts) and glycerol (18.5 parts) are heated with stirring in the presence of 0.05 part of sodium hydroxide for an hour at 250°C. Phthalic anhydride (43.8 parts) is then added in small portions and heating continued for about 5 hours at 200°C. until a resin of acid number of 55–60 results. The product is soluble in ethyl alcohol, toluene and butyl acetate and alcohol-hydrocarbon mixtures. A clear, pale resin can be prepared from ricineläidin, adipic acid and ethylene glycol. These resins, which are soluble in hydrocarbons, acetone and esters, can be used as softeners in nitrocellulose lacquers.

<sup>20</sup> T. F. Bradley, U. S. P. 1,785,980, Dec. 23, 1929, to Ellis-Foster Co.; *Brit. Chem. Abs. B*, 1931, 818.

<sup>21</sup> T. F. Bradley, U. S. P. 1,863,264, June 14, 1932; *Brit. Chem. Abs. B*, 1933, 478.

<sup>22</sup> German P. 609,705, 1935, to Firma Louis Blumer; *Chem. Abs.*, 1935, 29, 5201.

<sup>23</sup> H. A. Bruson, U. S. P. 1,783,187, Nov. 25, 1930, to Resinous Products & Chem. Co.; *Brit. Chem. Abs. B*, 1931, 644. British P. 363,859, 1930; *Chem. Abs.*, 1932, 27, 1774. German P. 555,082, 1930; *Chem. Abs.*, 1932, 26, 5228. French P. 705,069, 1930, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1931, 25, 5311.

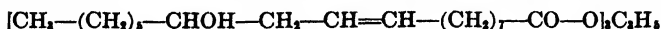
<sup>24</sup> H. A. Bruson, British P. 360,363, 1931; *Brit. Chem. Abs. B*, 1932, 671. French P. 706,913, 1930, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1932, 26, 479.

<sup>25</sup> F. F. Frick and K. Ott, German P. 557,812, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 617.

<sup>26</sup> M. M. Brubaker, U. S. P. 1,932,998, Oct. 31, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 664.

## TREATMENT OF CASTOR OIL WITH DIBASIC ACIDS

Castor oil,<sup>28</sup> which is essentially the glycerol ester of ricinoleic acid,



contains free hydroxyl groups and may be esterified with acids.<sup>27</sup> Oda<sup>28</sup> studied the reaction of phthalic anhydride and castor oil by heating the reactants at 190-245°C. in carbon dioxide and found that multimolecular compounds are formed. Citric and malonic acids react easily with castor oil whereas succinic and tartaric enter with difficulty. Castor oil with oxalic acid at 140-150°C. and 15 mm. pressure yields an acid ester as well as a condensation product of 2 mols of the oil to 1 mol of the acid.<sup>29</sup>

By heating 311 grams of castor oil and 100 grams of maleic acid for 18 hours at 110-120°C., a yellow, transparent gummy mass was obtained which was practically neutral and which was soluble in castor oil and in other oils under heat. In hot turpentine, a true solution is not formed but rather a viscous pseudo-solution.<sup>30</sup> Plastic materials are also obtained by reacting castor oil with the half-ester of maleic anhydride obtained by condensing equimolecular proportions of maleic anhydride with a monohydric alcohol (cyclohexanol, hexyl, capryl, benzyl alcohols, borneol,  $\alpha$ -terpineol, diethylene glycol monobutyl ether or octadecanol). The syrupy products prepared under these conditions are soluble in benzene, toluene, acetone, butyl acetate, petroleum naphtha and are compatible with nitrocellulose.<sup>31</sup>

Castor oil either free or hydrogenated can be condensed with phthalic anhydride by heating at 140°C. for 1 hour in such a manner that the acid ester is formed. On neutralization, metallic salts are obtained which are soluble in butyl alcohol, butyl or ethyl acetate and which are compatible with nitrocellulose. When incorporated into films, there is an improved fastness to light.<sup>32</sup> By carrying out the reaction at 220°C. with phthalic or maleic anhydride and castor oil, the compound may be used directly as a softening agent for nitrocellulose<sup>33</sup> or for the formation of nitrocellulose films.<sup>34</sup> Reaction can also be effected at 100°C. provided a condensing agent (zinc chloride) is used. The product is a pale yellow-brown oil.<sup>35</sup> Heating castor oil with phthalic anhydride to 150-180°C. yields a stiff oil which can also be mixed with cellulose esters.<sup>36</sup> Moore<sup>36a</sup> made a resinous product

<sup>28</sup> For the use of castor oil as a raw material for plasticizers and resins, see L. Light, *Chem. Age*, 1934, 30, 491; *Chem. Abs.*, 1934, 28, 4921. Treatment of castor oil with 0.5 per cent of an alkali metal oxalate or oxalic acid or its esters retards rancidification of the oil when used as a softener in nitrocellulose coating compositions. See T. H. Rogers, U. S. P. 1,826,258, Oct. 6, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 613.

<sup>27</sup> For the inner-esterification of castor oil and derivatives, that is, the formation of estolides, see Chapter 61.

<sup>28</sup> R. Oda, *J.S.C.I., Japan*, 1933, 36, 623; *Brit. Chem. Abs. A*, 1934, 171.

<sup>29</sup> R. Oda, *ibid.*, 1933, 36, 496, 571; *Brit. Chem. Abs. A*, 1933, 1275.

<sup>30</sup> K. Daimler, German P. 479,965, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 5018. When this material is mixed with the reaction product of maleic anhydride and butylene glycol, a composition suggested for use in safety glass is formed. See British P. 363,933, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1729. Cellulose derivatives can also be added. British P. 363,940, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 262. For the reaction of maleic anhydride and 1,3-butylene glycol, see K. Daimler and G. Balle, U. S. P. 1,984,671, Dec. 18, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 902.

<sup>31</sup> British P. 405,805, 1934, to the Resinous Products & Chem. Co.; *Chem. Abs.*, 1934, 28, 4949.

<sup>32</sup> C. Coolidge, U. S. P. 1,900,693, Mar. 7, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1933, 1017. See Chapter 46.

<sup>33</sup> H. J. Barrett, U. S. P. 1,933,697, Nov. 7, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 638.

<sup>34</sup> H. J. Barrett, U. S. P. 1,936,787, Jan. 8, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 1246.

<sup>35</sup> W. H. Glover and W. Berry, British P. 373,911, 1932, to Courtaulds, Ltd.; *Chem. Abs.*, 1933, 27, 4106.

<sup>36</sup> German P. 602,881, 1934, to Firma Louis Blumer; *Chem. Abs.*, 1935, 29, 855. See German P. 564,900, 1930; *Chem. Abs.*, 1935, 27, 1219 and German P. 580,263, 1933; *Chem. Abs.*, 1933, 27, 4943.

<sup>36a</sup> C. G. Moore, Canadian P. 348,040, 1935, to Glidden Co.; *Chem. Abs.*, 1935, 29, 3422.

for use in nitrocellulose lacquers by heating 186 parts castor oil and 30 parts succinic acid to 180°C., at which point condensation actively begins. The temperature was finally raised to 260-310°C. until the resin had an acid number of about 20.

Castor oil has also been esterified with the natural acidic resins. By heating rosin with castor oil or with ricinoleic acid *in vacuo* or in an inert atmosphere at 260°C., an acid-free viscous oil is obtained which acts as a softening agent for celluloid, casein or phenol-formaldehyde resins.<sup>37</sup> The castor oil fatty acids may first be dehydrated before esterification with natural resins. In this instance, however, glycerol should be added. Scheiber<sup>38</sup> in subjecting ricinoleic acid or the mixture of castor oil fatty acids to prolonged heating *in vacuo*, prepared an isomeric linoleic acid. This acid was first esterified with an excess of glycerol and the excess esterified with a resin acid (copal, rosin). On adding a diluent a varnish is obtained, the drying capacity of which may be regulated by the addition of driers. The same method can be used with a mixture of acids, for example those derived from semi- or non-drying oils together with ricinoleic acid.<sup>39</sup>

The resin of acid number 50 derived from glycerol (18 parts), phthalic anhydride (44 parts) and castor oil (38 parts) at 200°C. can be modified with polymerized terpene resins in the following proportions: 75 per cent of alkyd resin, 21.2 per cent of "polymerized terpene resin G"<sup>40</sup> and 3.8 per cent "polymerized terpene resin E."<sup>41</sup> An adhesive for laminated material is thus formed.<sup>42</sup>

Water-soluble products, used as wetting-agents in dyeing, are obtained by treating higher unsaturated fatty acids with a sulphonating agent in the presence of sulphonated aromatic carboxylic acids. Thus, castor oil or ricinoleic acid is treated with a mixture of phthalic acid anhydride- $\beta$ -sulphonic acid and sulphuric acid,<sup>43</sup> or with phthalic acid anhydride- $\beta$ -sulphonic acid *in vacuo* at 150-160°C.<sup>44</sup> The product of the latter process is used as a wetting and finishing agent for textiles. Wetting, penetrating, foaming and dispersing agents are also formed when aliphatic acids with more than 8 carbon atoms (ricinoleic and hydroxy-stearic acids) or aromatic acids ( $\beta$ -naphthoic acid) are sulphonated and esterified with glycol monomethyl or monoethyl ether.<sup>45</sup> The castor oil-modified glycerol phthalate of low acid number has also been employed in dressing textiles.<sup>46</sup>

#### RESINS FROM POLYHYDROXY ACIDS

Bruson<sup>47</sup> has utilized polyhydroxy acids for the preparation of alkyd-type resins. Acids available for the purpose include dihydroxystearic acid,  $C_{17}H_{33}(OH)_2COOH$ , trihydroxystearic acid,  $C_{17}H_{33}(OH)_3COOH$ , tetrahydroxystearic acid,  $C_{17}H_{33}(OH)_4COOH$ , hexahydroxystearic acid,  $C_{17}H_{33}(OH)_6COOH$ , and dihydroxybehenic acid,  $C_{21}H_{41}(OH)_2COOH$ , which may be obtained by regulated oxidation of the unsaturated oils by means of alkaline potassium permanganate.

These acids, containing two or more hydroxyl groups, may be condensed with polybasic acids, such as phthalic, succinic, maleic, adipic, diphenic, naphthalic acids

<sup>37</sup> British P. 329,958, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 213.

<sup>38</sup> J. Scheiber, U. S. P. 1,979,495, Nov. 6, 1934; *Chem. Abs.*, 1935, 29, 366. British P. 306,542, 1929; *Brit. Chem. Abs. B*, 1930, 726. See Chapter 47.

<sup>39</sup> J. Scheiber, British P. 306,453, 1930; *Brit. Chem. Abs. B*, 1930, 871.

<sup>40</sup> "Polymerized terpene resin G" is also known as "Flexoresin GG-1."

<sup>41</sup> "Polymerized terpene resin E" is also known as "Flexoresin E-1."

<sup>42</sup> J. E. Snyder, U. S. P. 1,902,249, Feb. 26, 1935, to Du Pont Cellograph Co., Inc.; *Chem. Abs.*, 1935, 29, 2827.

<sup>43</sup> German P. 535,854, 1930, to Soc. anon. pour l'ind. chim à Bâle; *Chem. Abs.*, 1932, 26, 1079.

<sup>44</sup> German P. 548,799, 1930, to Soc. anon. pour l'ind. chim à Bâle; *Chem. Abs.*, 1932, 26, 4184. Swiss P. 149,404, 1930; *Chem. Abs.*, 1932, 26, 4966.

<sup>45</sup> British P. 351,456, 1930, to H. T. Böhme A.-G.; *Brit. Chem. Abs. B*, 1931, 1003.

<sup>46</sup> German P. 605,573, 1934, to Firma Louis Blumer; *Chem. Abs.*, 1935, 29, 1999.

<sup>47</sup> H. A. Bruson, U. S. P. 1,815,886, July 21, 1931, to Röhm & Haas Co.; *Chem. Abs.*, 1931, 25, 5525. German P. 593,539, 1934, to Chem. Fabr. K. Albert, G.m.b.H.; *Chem. Abs.*, 1934, 28, 6004. See also German P. 611,056, 1935, to Chem. Fabr. K. Albert, G.m.b.H.; *Chem. Abs.*, 1935, 29, 4103.

and the like to form resins, which in turn may be modified by incorporating a proportion of fatty oils. As an example 9,10-dihydroxystearic acid (obtained by permanganate oxidation of oleic acid) is mixed with an equimolecular quantity of phthalic anhydride, and heated to 190°C. As condensation proceeds, the mixture yields a hard translucent wax, which eventually forms an oily liquid, becoming more viscous as heating is continued. On cooling, a rubbery mass is obtained which is soluble in acetone, but becomes insoluble on long heating. Incorporation of drying oils leads to viscous oily masses useful for coating compositions. In general, the products are suited for coating textiles, leather, rubber and thin sheet metal, where flexibility and waterproofness are prime requisites.

If, on the other hand, the polyhydroxy acids are esterified with alcohols, products can be prepared which serve as plasticizers for cellulose derivatives.<sup>48</sup> Glycols give rise to viscous oils, whereas glycerol or mannitol first yields a clear liquid, then a soluble rubbery material and finally an insoluble plastic mass.

A liquid acid portion of the oxidation of paraffin hydrocarbons,<sup>49</sup> which consists essentially of hydroxycarboxylic acids and which is insoluble in light petroleum, can be esterified with a polyhydroxy alcohol (glycol, glycerol) to yield a rubbery plastic composition. Before or during the heating process, siccatives (lead oxide, linoleic acid or linolein) may be introduced,<sup>50</sup> or air may be passed through.<sup>51</sup> Sulphur or sulphur monochloride can be added also. A similar class of substances results from the unsaturated acids of oxidized paraffin wax.<sup>52</sup> The carboxylic acids from the oxidation of paraffin hydrocarbons can be condensed with glycerol and phthalic anhydride to yield a resin.<sup>53</sup>

By heating a polyhydric alcohol with bleached montan wax, together with a monobasic fatty acid (coconut oil fatty acids,<sup>54</sup> ricinoleic acid),<sup>55</sup> an aromatic (salicylic) or a hydroaromatic acid,<sup>56</sup> and with or without an accelerator (sodium bisulphate, boric acid, or anhydrous zinc chloride), products are obtained which resemble natural waxes. Any free acid is converted into an ester, an amide or a salt. Fillers, dyes, gums, plasticizers and other resinous compounds may be added and the final material is pressed and heated after comminution.<sup>57</sup> Montan wax can also be treated with glycerol in the presence of sodium hydroxide or lead oxide. The resulting composition can then be esterified with phthalic anhydride, rosin, and drying oil acids.<sup>58</sup>

#### EFFECT OF NATURAL RESINS

By the incorporation of certain other constituents both the properties and the applications of alkyd resin products are altered considerably. When the added ingredient is a natural resin the alkyd resins so modified are well known under the name "Teglac,"<sup>59</sup> (see Fig. 127) and some products of the Teglac type approxi-

<sup>48</sup> H. A. Bruson, U. S. P. 1,835,203, Dec. 8, 1931, to Röhm & Haas Co.; *Brit. Chem. Abs. B*, 1932, 902.

<sup>49</sup> For the oxidation of paraffin wax see Carleton Ellis, "Chemistry of Petroleum Derivatives," Chemical Catalog Co., Inc., N. Y., 1934.

<sup>50</sup> M. Luther and R. Held, U. S. P. 1,884,023 and 1,884,024, Oct. 25, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1222. German P. 575,954, 1933; *Chem. Abs.*, 1933, 27, 4890. British P. 322,496, 1928; *Chem. Abs.*, 1930, 24, 2904.

<sup>51</sup> British P. 327,094, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5172.

<sup>52</sup> M. Luther and H. Reller, U. S. P. 1,897,133, Feb. 14, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2845. British P. 323,580, 1928; *Chem. Abs.*, 1930, 24, 3134. French P. 676,659, 1929; *Chem. Abs.*, 1930, 24, 3185. See also French P. 764,948, 1934; *Chem. Abs.*, 1934, 28, 6003.

<sup>53</sup> G. V. Mitvitskii and B. V. Makarov, Russian P. 27,789, 1931; *Chem. Abs.*, 1933, 27, 2331.

<sup>54</sup> W. Punga and K. Behringer, U. S. P. 1,825,248, Sept. 29, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 329.

<sup>55</sup> W. Punga and K. Behringer, U. S. P. 1,825,249, Sept. 29, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 329.

<sup>56</sup> British P. 324,631, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 519.

<sup>57</sup> British P. 327,718, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 780.

<sup>58</sup> British P. 417,577, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1934, 1110.

<sup>59</sup> Teglaacs are products of the American Cyanamid Co.

mate in their physical properties those of the natural resins. For the most part, however, they lack the toughness of alkyd resins made with oil modifying agents and generally are not recommended for use alone in coating compositions. They are, nevertheless, more truly compatible with nitrocellulose than the greater part of the natural resins. Hence the Teglac materials have a wide use in lacquer preparations. They have also been cooked into varnish, and incorporated into enamel and paint products.<sup>60</sup>

Natural-resin-modified alkyds are easily soluble in cold toluene, in turpentine, in Cellosolve and in similar solvents, and are suited for the production of glossy brushing lacquers. Their exceptionally high index of refraction imparts a gloss and a depth of film similar to that secured with oleo-resinous varnishes. Blending of a proportion of the natural-resin-alkyd with a drying oil-alkyd lacquer results



FIG. 127.

Fragment of Teglac Which Shows a Peculiar Conchoidal Fracture.

in improved hardness to the latter; for this reason the former are especially well adapted to the production of sanding sealers.<sup>61</sup>

Metallic driers cannot, as a rule, be incorporated with rosin-phthalic glyceride varnishes by the common process of adding the accelerator to the bodied oil and resin at about 200°C. Precipitation occurs either at once or upon aging, regardless of whether linseed or tung oil is used; the drier is removed from solution by the acid constituents present in the resin. The driers may, however, be added to the cold varnish, in the form of their solutions in oil, without any precipitation ensuing. This tendency to precipitate the added metallic driers may be partially overcome by removing free phthalic anhydride from the resin.

Resins, which are soluble in acetone, in acetone-alcohol or in acetone-benzene mixtures and which blend with nitrocellulose to yield good films, are formed by incorporating rosin in a glycerol phthalate resin. A resin of this type is formed<sup>62</sup> when 50 parts of phthalic anhydride, 33 parts of glycerol and 75 parts of light-colored rosin are heated to 250°C. To the clear product thus formed (acid number 68), 10 parts of glycerol are added, and further heated to 290°. A clear transparent resin is produced, somewhat darker than the original rosin,

<sup>60</sup> M. R. Trimmer and J. M. Sanderson, *Paint, Oil, Chem. Rev.*, 1931, 91 (23), 19; *Chem. Abs.*, 1931, 25, 3334.

<sup>61</sup> For the use of Lewisol No. 18 resin as a quick-drying sanding sealer see *Paint, Oil, Chem. Rev.*, June 14, 1934, 33.

<sup>62</sup> Carlston Ellis, U. S. P. 1,732,566, July 30, 1929; *Chem. Abs.*, 1929, 23, 4533.



and having an acid number of 12.7. The use of 100 parts of rosin, 15 parts of phthalic anhydride and 25 parts of glycerol heated to 290°, yields a hard resin of acid number 7.7.

In the preparation of such resins, lime, zinc oxide or baryta may be added. The basic substances produce a hardening effect, inasmuch as they combine with any free acid. (See Chapter 37.) If the resin, after the addition of the bases, be heated until combination with free acid is complete, the acid number of the final product may be reduced to a low value. A mixture of equal parts of shellac, glycerol and phthalic acid heated to 295°C. yields a dark resin which softens at about 60°C. to a rubbery mass, and ultimately fuses between 120° and 150°C.

An important property of the rosin-phthalic glyceride resins is that already mentioned, that is, their compatibility in all proportions with nitrocellulose.<sup>62</sup> Addition of as little as 5 per cent of nitrocellulose or celluloid (conveniently in the form of scrap motion-picture film) greatly improves the toughness of the resins. By using a higher proportion of nitrocellulose the toughness is still further enhanced, so that a resin containing 25-30 per cent of nitrocellulose in a solvent may be poured out onto glass and will dry to a clear coherent film which may be removed in its entirety. Such hardened resins may be used as varnishes or japans, as substitutes for hard rubber and for tough transparent sheets, although the color of the natural-resin-modified alkyd is not as light as that of good quality nitrocellulose. The presence of a considerable or preponderant proportion of rosin-phthalic glyceride apparently reduces the inflammability of the nitrocellulose, and the latter in turn increases the water-resistance of the resin. An example of a coating for floors is that produced by dissolving 25 parts of rosin-phthalic glyceride resin and 50 parts of scrap motion-picture film in a mixture of 50 parts of benzene and 100 parts of acetone. The viscous solution dries to a tough, transparent, light-yellow film. Congo copal can be used to replace the rosin in the rosin-glycerol phthalate resins; the copal-alkyds are also compatible with nitrocellulose.<sup>64</sup>

For blending with nitrocellulose, it is advantageous to employ products of an acid number less than 20 and devoid of free glycerol.<sup>65</sup> The latter being hygroscopic, tends to give rise to turbidity or to "blushing" of the film. The function of the natural resins, co-esterified with a polyhydric alcohol-polybasic acid resin, is to produce soluble, water-resistant resins of low acid number. Although natural resins<sup>66a</sup> of various kinds such as copal, manila or dammar, may be used in conjunction with the various possible combinations of alkyd resins, the low cost and wide range of useful properties has led to the greatest development of rosin-glycerol phthalate resins. A useful resin fulfilling the above conditions, that is, of low acid number and the absence of free glycerol, is made by heating 1340 parts of WW rosin, 308 parts of phthalic anhydride and 348 parts of glycerol, with agitation, to 290°, until the acid number of a test sample is below 20. The product is light-colored and soluble in benzene. It contains the equivalent of 3 parts of rosin glyceride to 1 part of phthalic glyceride reacted together in such a manner as to form a homogeneous resin complex. Such compositions may be given an increased flexibility and improved adhesion, when employed in conjunction with nitrocellulose, by incorporating a softening agent such as castor oil, diethyl phthalate or, less appropriately, triacetin. A coating composition may be derived from 3 parts of the above resin and 2 parts of low-viscosity nitrocellulose in the form of a 50 per cent solution.

The acid number may further be reduced by neutralization of the resin with

<sup>62</sup> H. M. Weber, U. S. P. 1,722,776, July 30, 1929, to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 4582.

<sup>64</sup> H. M. Weber, U. S. P. 1,787,104, May 6, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1930, 24, 3595.

<sup>65</sup> Carleton Ellis, U. S. P. 1,843,869, Feb. 3, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 26, 1812.

<sup>66a</sup> Carleton Ellis, U. S. P. 2,000,937, May 14, 1935, to Ellis-Foster Co.

aromatic amines.<sup>66</sup> Thus, 100 parts of a resin prepared as above (acid number 10.9) when heated at 290°C. with 5 parts of p-toluidine, yielded a product of acid number 4.9. By the use of 10 parts of the amine, the acid number was reduced to zero. The complete absence of free acid is advantageous in some molding compositions, and, in certain cases, in nitrocellulose lacquers. Phthalic glyceride resins of high acid number, which tend to become infusible on heating, may have their acid number considerably reduced, and at the same time their heat-convertibility subdued, by this method of amine neutralization. Fusible shellac substitutes may be made in this manner.

By a process of controlled atmospheric oxidation, the melting point of resins of this nature may be raised.<sup>67</sup> In the case of a rosin-phthalic glyceride which softened initially at 90°C., the softening point was raised to 99°C. by four days' heating at 50°, finally reaching 105°C. after a further two days' heating at 60°. The procedure is to heat the powdered resin in a shallow layer, at a temperature somewhat below the fritting point. With certain synthetic resins the oxidation may proceed to a point where insolubility occurs, although this is not the case with the rosin-phthalic glyceride. On the contrary, the resin becomes more soluble in lacquer solvents, and is rendered more valuable for the production of hard lacquer coatings. It is also feasible to incorporate catalysts (lead resinate) in the original resin to accelerate the oxidation process.

Resins of a lower melting point than an unmodified rosin-phthalic glyceride may be made by introducing a monobasic acid<sup>68</sup> such as benzoic. The property of compatibility with cellulose esters is thus retained, whereas the toughness and adhesion of the lacquer film are enhanced. The quantity of plasticizer may frequently be reduced when such resins are employed. Moreover, the employment of low-melting resins with nitrocellulose in plastic compositions decreases the danger of decomposing the cellulose ester. By appropriate choice of the organic acid, the softening point may, on the other hand, be raised, giving rise to harder films.

The incorporation into glycerol phthalate of fatty acids (stearic, dihydroxystearic) or aromatic monobasic acids (toluylbenzoic, benzoylbenzoic) and natural resins (rosin or Congo copal)<sup>69</sup> leads to the formation of light-colored products which are soluble in lacquer solvents and compatible with nitrocellulose. In these lacquers the nitrocellulose is not the chief constituent, but only a toughening and hardening agent. Substitution of pentaerythritol, or di- or triethylene glycol, for glycerol is advantageous in that it facilitates the formation of more homogeneous products. A resin illustrative of this type is produced by heating at 290°C. 45 parts of stearic acid, 45 parts of fused or "run" Congo resin, 74 parts of phthalic anhydride and 58 parts of pentaerythritol. The addition of small amounts of basic substances (urea) prevents the formation of insoluble substances from mixes which contain a large proportion of phthalic anhydride; the latter may be partly replaced by a monobasic acid. Resins from glycerol and polybasic acids, modified with copal, kauri, dammar or resin acids<sup>70</sup> or with cottonseed oil acids,<sup>71</sup> may be used with a lesser proportion of cellulose ester for coating compositions.

Bradley<sup>72</sup> sought to overcome the use of nitrocellulose entirely in lacquer compositions by using waxy substances in the alkyd resins. He first prepared a cottonseed acid-modified glycerol phthalate in the ratio of 90-100-160 respectively, and

<sup>66</sup> Carleton Ellis, U. S. P. 1,843,870, Feb. 2, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1932, 26, 1812.

<sup>67</sup> Carleton Ellis, U. S. P. 1,872,568, Aug. 16, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1932, 26, 6165.

<sup>68</sup> H. M. Weber, U. S. P. 1,897,018, Feb. 7, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 2890.

<sup>69</sup> Carleton Ellis, U. S. P. 1,900,638, Mar. 7, 1933; *Brit. Chem. Abs. B*, 1933, 1022.

<sup>70</sup> British P. 327,095, 1923, to Ellis-Foster Co.; *Chem. Abs.*, 1930, 24, 5172. French P. 667,918, 1929; *Chem. Abs.*, 1930, 24, 1529.

<sup>71</sup> British P. 327,096, 1923, to Ellis-Foster Co.; *Chem. Abs.*, 1930, 24, 5172. French P. 667,919, 1929; *Chem. Abs.*, 1930, 24, 1529.

<sup>72</sup> T. F. Bradley, U. S. P. 1,933,583, Apr. 3, 1934, to American Cyanamid Co.; *Chem. Abs.*, 1934, 28, 3907.

then mixed 1 part of this resin with 5 parts of rosin ester and 0.3 part of spermaceti wax in 22 parts of toluene. Cetyl alcohol ( $\text{CH}_2-(\text{CH}_2)_{11}-\text{CH}_2\text{OH}$ ), the hydrolytic product of spermaceti wax, may also be incorporated into the rosin-modified glycerol phthalate.<sup>74</sup>

#### FURTHER MODIFICATION OF NATURAL RESIN ALKYDS

Bruson<sup>74</sup> has developed a process of esterifying rosin or other natural resins with glycerol and the straight-chain aliphatic dibasic acids such as adipic acid and higher homologues. The products are unusually tough and flexible, and maintain their flexibility down to  $-5^\circ\text{C}$ . They are compatible with cellulose esters. An example of this variety is the resin produced by heating 30 parts of rosin with 15 parts of sebacic acid and 5 parts of glycerol to  $200^\circ\text{C}$ ., finally raising the temperature to  $260^\circ\text{C}$ . Increase in the proportion of colophony increases the hardness. A similar composition, but containing 15 parts of glycerol, has been cited as giving a transparent, flexible and very elastic layer useful for photographic films or as a coating composition for leather, fabrics and rubber.<sup>75</sup> The resin derived from 95 parts of glycerol, 150 parts of rosin and 148 parts of adipic acid at  $280^\circ\text{C}$ . has been described by Sellet<sup>76</sup> as useful for paint, varnish and lacquer production.

Bruson<sup>77</sup> has also made application of the high-melting relatively insoluble and non-volatile benzophenone polycarboxylic acids with regard to resin formation, and has obtained very hard, water-resisting products of high melting point. The ketonic acids, especially benzophenone-2,4'-dicarboxylic acid, appear to be adaptable for this purpose. Seventy-five grams of benzophenone dicarboxylic acid were heated with 150 grams of rosin and 35 grams of glycerol to  $250^\circ\text{C}$ . for 4.5 hours to yield a benzene-soluble resin which melted at  $120$ - $130^\circ\text{C}$ . Darkening of the product may be avoided by allowing the esterification to take place in a nitrogen atmosphere. Related acids, such as 2,2'-dinaphthyl-1,1'-dicarboxylic acid, or 2,2'-di(biphenylketone)dicarboxylic acid, or tri- or tetrabasic benzophenone carboxylic acids give resins of similar properties. When 238 grams of dihydroxydiphenylmethane are heated with 123 grams of glycerol, a soft, colorless, sticky, partially esterified compound is formed. Subsequent reaction with 600 grams of rosin at  $290^\circ\text{C}$ . yields a clear, brittle resin soluble in fatty oils, esters, acetone and benzene.<sup>78</sup>

A rust-preventing paint can be produced by mixing rosin-modified glycerol phthalate with oils and pigments.<sup>79</sup> The clear resin (softening point  $85^\circ\text{C}$ .) is prepared by treating colophony with glycerol and then condensing with phthalic anhydride at  $250^\circ\text{C}$ .<sup>80</sup>

The co-esterification of phthalic (or other polybasic) acid and resin acids, in the form of colophony, rosin oils or abietic acid, with glycerol has also been applied by Yeates<sup>81</sup> to the production of hard, high-melting resins soluble in lacquer

<sup>74</sup> T. F. Bradley, U. S. P. 1,951,593, Mar. 20, 1934, to American Cyanamid Co.; *Brit. Chem. Abs. B*, 1935, 92.

<sup>75</sup> H. A. Bruson, U. S. P. 1,783,165, Nov. 25, 1930, to Resinous Products & Chem. Co.; *Chem. Abs.*, 1931, 25, 424.

<sup>76</sup> H. A. Bruson, British P. 341,477, 1929, to Chem. Fabr. K. Albert G.m.b.H.; *Brit. Chem. Abs. B*, 1931, 452. See French P. 766,855, 1934; *Chem. Abs.*, 1934, 28, 7564.

<sup>77</sup> L. Sellet, French P. 697,968, 1931; *Chem. Abs.*, 1931, 25, 3186.

<sup>78</sup> H. A. Bruson, U. S. P. 1,829,038, Oct. 27, 1931, to Röhm & Haas Co.; *Chem. Abs.*, 1932, 26, 861.

<sup>79</sup> O. A. Cherry, U. S. P. 1,962,788, Dec. 4, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 523.

<sup>80</sup> K. Ott, F. Frick and H. Bernard, German P. 553,512, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5776.

<sup>81</sup> K. Ott, F. Frick and H. Bernard, German P. 547,517, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3686.

<sup>82</sup> R. L. Yeates, British P. 306,924, 1927, to Grindley & Co., Ltd.; *Chem. Abs.*, 1929, 23, 5339.

solvents. Fatty acids from drying oils (linseed or tung oil) or from non-drying oils (oleic or stearic acids) may also be incorporated. When the quantity of glycerol employed is less than the chemical equivalent, inorganic basic materials may be added, if desired, to lower the acid number. A modification of the method lies in condensing a polybasic acid, together with an acid resin, with an excess of a polyhydric alcohol in the presence of cyclohexanol or methyl cyclohexanol.<sup>82</sup>

Durr<sup>83</sup> modified the process of co-esterification of glycerol, phthalic anhydride and natural resins and obtained a product of acid number 2-4 which may be heated indefinitely at 250° without becoming insoluble. When pulverized, the resin is a white- to brown-colored powder, very readily soluble in esters and in the usual cellulose lacquer solvents. The method consists in heating glycerol with phthalic acid and with natural resin, the total amount of acid taken being insufficient to esterify the glycerol completely. A resin of this nature is produced by taking 285 parts of phthalic anhydride and 200 parts of colophony with 240 parts of glycerol and heating gradually for 15-20 hours until the temperature reaches 260°C., then maintaining the melt at this temperature for 2 hours. The product melts at 105-120°C., as measured by its Ubbelohde dropping point. By heating a similar mixture to 290°C., a resin of Ubbelohde dropping point 130-138°C. is obtained.

Another process developed by Durr<sup>84</sup> consists in condensing a natural resin with glycerol, or of already formed resin esters, with previously formed glycerol phthalate resins. Condensation takes place above 200°C., the entire mixture becoming soluble in ethyl acetate, and yielding products stated to be analogous to, but not identical with, those formed by simultaneous esterification. An example cited is as follows. To 100 grams of colophony at 250°C. are added 100 grams of Congo gum and 4 grams of glycerol, the whole being heated until limpid. The resin ester so made is then introduced at 170°C. into a product made from 200 grams of glycerol and 285 grams of phthalic anhydride, finally heating for 4 hours at 260°C. The final product is soluble in esters and in mixed solvents.

Synthetic resins useful in heat-resistant molded articles or as cements for mica and similar materials, are produced by the reaction of Congo resin and a polybasic acid with polyhydric alcohols.<sup>85</sup> By heating to 230°C. 1000 grams of Congo copal, 247 grams of phthalic anhydride and 203 grams of glycerol, a resin is obtained which may either be dissolved in benzene or toluene or mixed with a filler and molded. Substitution of rosin for one-half of the Congo gives a more fusible, brittle, quick-setting product. The use of 920 grams of rosin with 740 grams of phthalic anhydride and 420 grams of glycerol yields a hard, tough resin which hardens less rapidly.

The low degree of resistance to water, which frequently constitutes a disadvantage to the use of glycerol phthalate or modified glycerol phthalate resins, is said to be overcome by the incorporation of shellac.<sup>86</sup> The process may be applied either to the initial soluble stage of the polybasic acid-polyhydric alcohol condensation, to the intermediate insoluble stage or even to the final infusible condensation product. The shellac may be dissolved in the same solvent, or powdered and intimately mixed in the case of hot-molding compositions.<sup>87</sup> The products, con-

<sup>82</sup> R. L. Yeates, British P. 331,422, 1933, to Grindley & Co., Ltd.; *Chem. Abs.*, 1933, 27, 4111. French P. 746,577, 1933; *Chem. Abs.*, 1933, 27, 4702.

<sup>83</sup> A. H. V. Durr, U. S. P. 1,739,448, Dec. 10, 1929, to Compagnie nationale Nord reunies (Étab. Kuhlmann); *Chem. Abs.*, 1930, 24, 932. British P. 303,336, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 4533.

<sup>84</sup> A. H. V. Durr, U. S. P. 1,739,448, Dec. 10, 1929, to Compagnie nationale Nord reunies (Étab. Kuhlmann); *Chem. Abs.*, 1930, 24, 932. British P. 303,336, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 4534.

<sup>85</sup> T. F. Bradley, U. S. P. 1,722,554, July 30, 1929; *Chem. Abs.*, 1929, 23, 4533.

<sup>86</sup> L. Weisberg, U. S. P. 1,418,145, Apr. 18, 1923, to Barrett Co.; *Chem. Abs.*, 1922, 16, 2233.

<sup>87</sup> A. Haroldson has described the incorporation of shellac with alkyl resins to yield compositions

taining about one-half of their weight of shellac, are water-resistant and may replace shellac for many purposes. Shellac may also be incorporated into a natural rosin-modified alkyd in the presence of zinc oxide.<sup>88</sup>

Useful conversion products have been obtained by reacting natural resins and their esters with phenols in the presence of boron fluoride or hydrogen chloride.<sup>89</sup> The method has been extended to alkyd resins modified with natural resin acids. Alternatively, the natural resins or natural-resin-alkyd combinations may be treated alone in inert solvents with volatile halides, such as aluminum, titanium or tin chlorides.<sup>90</sup> Another modification consists in dissolving a natural resin in an aromatic hydrocarbon and treating the solution with aluminum chloride. The product can be incorporated in alkyd resins.<sup>91</sup>

which may be used as a flexible cement (U. S. P. 1,999,097, Apr. 23, 1935, to Continental Diamond Fibre Co.) or which may be rendered insoluble and infusible by the application of heat and can be employed in the production of molded articles or electrical insulation (U. S. P. 1,999,096, Apr. 23, 1935, to Continental Diamond Fibre Co.).

<sup>88</sup> W. A. Boughton, U. S. P. 1,953,951, Apr. 10, 1934, to New England Mica Co.; *Chem. Abs.*, 1934, 28, 3920.

<sup>89</sup> French P. 734,390, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1221.

<sup>90</sup> British P. 399,206, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 1021. French P. 734,525, 1932; *Chem. Abs.*, 1933, 27, 1113.

<sup>91</sup> British P. 421,542, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 3748.

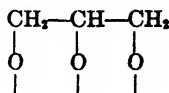
## Chapter 44

### Modified Alkyd Resins II. Use of Drying Oils and Acids

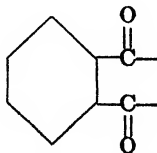
A distinct class of modified polyhydric alcohol-polybasic acid resins includes those containing a drying oil component. That is, a monobasic drying oil acid (e.g., linoleic acid) is embodied in the molecule to yield a resin possessing properties that differ from those of other alkyd resins.<sup>1</sup>

Solutions of the different alkyd resins thus far described produce films which at ordinary temperatures retain for a long time the properties of the original resin, and which may, or may not, be hardened by heat. Alkyd resins modified by the addition of certain unsaturated monobasic acids form films which harden rapidly at ordinary temperatures in the same way as drying oils or oil varnishes. The hardening of the film is caused principally by aerial oxygen and is catalyzed by the addition of compounds of lead, cobalt and manganese. The property of hardening at ordinary temperatures differentiates these resins as a class from those that do not undergo this change. Kienle and Ferguson<sup>2</sup> showed this distinction by classifying them as oxygen-convertible resins in contrast to those, such as phthalic glyceride and alkyd resins modified by adding only a small amount of monobasic acid, which require heat to harden them (heat-convertible resins), and those that do not harden under heat, such as the resin from phthalic anhydride and glycol or a phthalic-glyceride resin modified by adding a high proportion of a non-drying acid (non-convertible resins).

Oxidizing alkyds are formed by a deep-seated reaction between the raw materials, which brings the drying oil component into chemical combination with the resin-molecule. If —G— represents a glycerol molecule with the three hydrogen atoms of the hydroxyl groups replaced,



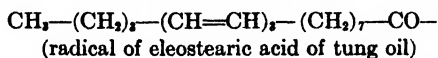
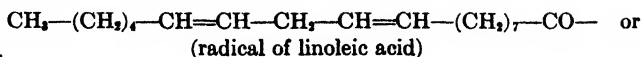
—P— represents the phthalyl radical,



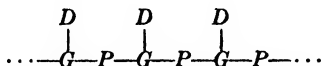
<sup>1</sup> All resins containing a polyhydric alcohol and a polybasic acid are called "alkyd" resins, even if they contain one or more monobasic acids or monohydric alcohols. For purposes of classification, however, the simple term alkyd resin is generally used to designate two-component resins, and when other reactants are added, the products are usually referred to as modified alkyd resins.

<sup>2</sup> R. H. Kienle and C. S. Ferguson, *Ind. Eng. Chem.*, 1929, 21, 349. See also H. H. Morgan, *J. Oil Colour Chem. Assoc.*, 1932, 15, 106; *Chem. Abs.*, 1932, 26, 3941; *Chem. Age (London)*, 1932, 26 (664), 256.

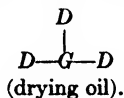
and D— represents the radical of a drying oil acid



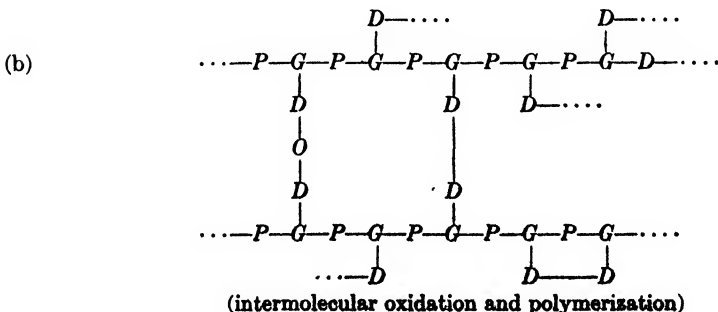
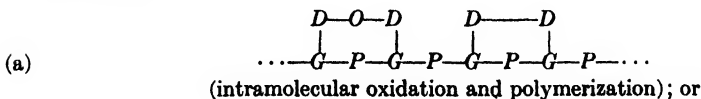
then the molecular structure of the resin may be represented in a more or less idealistic manner thus:



Of course, this applies only when equimolecular quantities of the reactants are used. If less of the drying oil component (*D*) is used, more of the glyceryl radicals (*G*) tend to unite with phthalyl (*P*), thus approaching the structure of phthalic glyceride. If more than one molecular quantity of (*D*) is used, more of the glyceryl groups (*G*) are combined with radicals of the drying oil acid and the structure approaches as an upper limit that of the drying oil itself,



Oxygen reacts with the unsaturated linkages of the drying oil component both additively (oxidation) and catalytically by inducing linkage between the double-bonds of the drying oil component (polymerization). This cross-linkage of the drying oil radicals may occur either, (a) in the same molecule (intramolecular oxidation and polymerization), (b) between two or more resin-molecules (intermolecular oxidation and polymerization). The latter yields infusible and more or less insoluble products by air-drying films of the resin. Oxidation may be represented in the resin molecule by  $-D-O-D-$ , and oxygen-induced polymerization by  $-D-D-$ , so that the structural formula for the final hardened resin becomes:

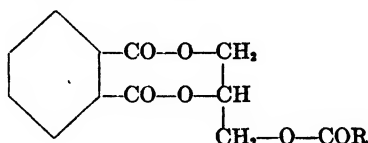


The result is a three-dimensional molecule of very large size.

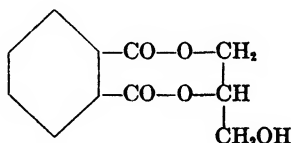
Drying oil alkyd resins dry faster than ordinary oil varnishes. This pro-

nounced drying property is somewhat of an anomaly when these resins are compared with the behavior of other derivatives of drying oils. The free fatty acids of drying oils do not dry. They oxidize, darken and become more viscous on exposure to the air but do not form a solid film.<sup>3</sup> Also the monohydric alcohol esters do not dry.<sup>4</sup> They absorb oxygen but remain liquid. Replacing glycerol in a drying oil by ethylene glycol gives an oil which dries more slowly than the original oil and produces a softer film; however, it forms a fairly tough film on baking. The glycol ester of tung oil acids yields an oxidation product which is a dark brown, tacky gel.<sup>5</sup>

It may be noted that the simplest formula for a resin from 1 mol phthalic anhydride, 1 mol glycerol and 1 mol drying oil acid (RCOOH) may be written:



This may be looked upon as the drying oil fatty acid ester of the monohydric alcohol:



However, as mentioned above, the usual monohydric alcohol esters of drying oil acids do not dry, whereas the drying oil alkyd does. From a consideration of derivatives of drying oil acids other than the oxidizing alkyds, it might be concluded that the oxidation of drying oil acid radicals to form hard films requires a combination of glycerol and drying oil acids as is present in the natural drying oils and that any variation in this arrangement results in poor drying. The pronounced film-forming properties of this type of drying oil derivative refutes that view. Nevertheless the result is unexpected and surprising.

Besides being molecularly of a different nature, drying oil-alkyd resins also show a contrast with ordinary oil varnishes in being more durable. Films of the resins dry rapidly, have excellent adhesion and are tough and flexible. Scheiber<sup>6</sup> has stated that the future of oil varnishes lies in the further development of the alkyd resin-oil combinations.

#### PRODUCTION OF DRYING OIL RESINS

Drying oil fatty acid radicals may be incorporated with the alkyd resin base in several ways. The free fatty acids obtained by hydrolysis of drying oils are most commonly used, and, when mixed with phthalic anhydride and glycerol, form an oily layer on top of the heated reaction mixture with which it gradually

<sup>3</sup> See R. S. Morrell and H. R. Wood, "The Chemistry of Drying Oils," D. Van Nostrand Co., New York, 1924, 21, 27.

<sup>4</sup> E. Fonrobert and F. Pallaut, *Chem. Umschau Fette, Oele, Wachse, Harze*, 1926, 33, 41; *Chem. Abs.*, 1926, 20, 2418.

<sup>5</sup> A. D. Miller and E. Claxton, *Ind. Eng. Chem.*, 1928, 20, 43. See also B. D. Thurman and W. R. Crandall, *ibid.*, 1928, 20, 1390.

<sup>6</sup> J. Scheiber, *Farben u. Lack*, 1932, 55, 73; 1934, 576, 330; *Chem. Abs.*, 1932, 26, 2331; 1934, 28, 6325.



(more rapidly when stirred) reacts to form a homogeneous melt. Sometimes it is possible to use the drying oils themselves, but on account of the immiscibility of drying oils and phthalic glyceride, the extreme slowness of reaction and the danger of gelatinization, it is usually\* advisable to modify the drying oil in some way first. This can be done by preheating the oil with glycerol or with the polybasic acid, or the glycerol can be modified to form ethers and esters, or be replaced by a glycol. Other ways of incorporating drying oils consist of mixing them with some of the drying oil acids or with a natural resin which acts as a flux and facilitates combination.

#### USE OF DRYING OIL FATTY ACIDS

Kienle<sup>†</sup> was the first to prepare a drying oil resin. He gradually heated a mixture of 92 parts by weight of glycerol and 296 parts of phthalic anhydride. When the temperature had reached 160°C. and a clear solution had formed, he introduced 140 parts of the fatty acid derived from a drying oil and an additional 74 parts of phthalic anhydride. Heating was continued at around 200°C. until frothing had ceased and a clear liquid had formed. The resin may also be made in a one-stage process by heating the entire mixture until the resin has formed, the correct degree of resinification being quickly determined by the stringing out of the product when it is allowed to fall in drops at a temperature of about 180°C. Resins of this type are soluble in acetone, alcohol-benzene mixtures, coal tar hydrocarbons, acetone oil, butyl acetate, butyl alcohol, ethyl lactate, glycol diacetate, glycol, glycol ethers, benzyl acetate, diethyl phthalate and triacetin. Upon air drying, the resin becomes hard, insoluble and infusible.

Weber<sup>‡</sup> found use for the fatty acids of soya bean oil. He heated a mixture of 94 parts of glycerol, 160 parts of phthalic anhydride and 80 parts of soya bean oil acids to a temperature of 265°C. and obtained a somewhat dark resin softening at 71°C. and having an acid number of 17. This resin was soluble in butyl acetate and butyl alcohol and easily miscible with nitrocellulose.

The fatty acids derived from walnut oil were employed by Bradley<sup>§</sup> in proportions of from 20 to 60 per cent by weight of the total mixture. Two hundred and thirty parts of the walnut oil fatty acids (which may be thickened by preheating), 148 parts of phthalic anhydride and 110 parts of glycerol were gradually heated (40 minutes) to 260°C. and the mixture held at from 270-290°C. for an additional 30 minutes. The resin is soluble in the ordinary paint and lacquer solvents and produces a harder and more durable film after drying; it may also be baked to a higher temperature with no material amount of discoloration or darkening; this allows both a longer baking period and a higher temperature. The finished product does not discolor with time. Lead oxide can be added to the oil-modified alkyd resin. Phthalic acid, 46.31 parts, 30.96 parts of linseed oil acids and 22.73 parts of glycerol are heated at 200°C. for 3 hours and allowed to cool to 170°C. Then about 10 per cent by weight of litharge is incorporated while the temperature is

\* R. H. Kienle, U. S. P. 1,893,873, Jan. 10, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 2319. British P. 284,349, 1927, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1928, 22, 4844. French P. 654,175, 1928, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 3332. Canadian P. 292,344, 1929, to Canadian General Electric Co., Ltd. Belgian P. 654,175, 1928, to La Société d'Electricité et de Mécanique. The Kienle Patent is one of a group of patents formerly involved in a controversy between General Electric Co., E. I. du Pont de Nemours Co., American Cyanamid Co. and Ellis-Foster Co. Arrangements were subsequently made looking to a cessation of hostilities. Later, a suit was brought by General Electric Co. against Paramet Chemical Co. of Brooklyn for infringement of this patent (U. S. District Court, Eastern Dist. of N. Y., Equity No. 7192), *Ind. Eng. Chem., News Ed.*, 1935, 13, 24; *Paint, Oil, Chem. Rev.*, 1935, 16. In this case the patent was declared invalid. See *Ind. Eng. Chem., News Ed.*, 1935, 13, 214.

† H. M. Weber, U. S. P. 1,690,515, Nov. 6, 1928, to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 513.

‡ T. F. Bradley, British P. 395,899, 1933, to American Cyanamid Co.; *Brit. Chem. Abs. B*, 1933, 837.

maintained at 170°C. The mixture is thinned with 150 parts of solvent naphtha and centrifuged to remove excess litharge and other impurities.<sup>10</sup>

Dawson<sup>11</sup> made a drying oil resin by using drying oil fatty acids but carried out the reaction in the presence of a small amount of concentrated sulphuric acid. The resin obtained in this way becomes hard and insoluble more quickly than without the acid. He added 10 cc. of concentrated acid to a mixture of 92 parts of glycerol and 200 parts of phthalic anhydride, and heated the mass to about 120°C. At this point much foaming occurs, water vapor and sulphur dioxide are given off and the mixture turns brown. After the rather violent reaction has subsided, about 70 parts of eleostearic acid (from tung oil) are added. This acid forms a distinct upper layer but dissolves as heating is continued. The product is a dark red mass, soluble in coal-tar hydrocarbons and in esters. It forms an adherent, water-resistant coating when applied to metals. Baking the coating for 30 minutes at about 210°C. causes it to harden. Scheiber<sup>12</sup> found that about 1 per cent of benzidine, diphenylamine or phenylenediamine facilitates the combination of drying oil fatty acids with phthalic anhydride and glycerol.

Resins of lighter color can be made by carrying out the reaction in the presence of an inert gas. Ninety-two parts by weight of glycerol, 148 parts of phthalic anhydride and 298 parts of linseed oil fatty acids, heated in an atmosphere of carbon dioxide to a temperature of 220°C. and held at this point for about 7 hours, produce a soluble, light-colored resin which hardens by oxidation. The addition of metallic driers accelerates oxidation and yields quick-drying varnishes whose films harden in about an hour.<sup>13</sup> Another related resin is obtained by heating 176 parts of glycerol, 288 parts of phthalic anhydride, 402 parts of linseed oil acids and 134 parts tung oil acids. This resin is dissolved in a hydrocarbon solvent and lithopone is ground into the solution to form an enamel for printing linoleum. The coating is hardened by drying at about 60°C. for 30 hours.<sup>14</sup> A further modification involves the use of glycol, phthalic anhydride and tung oil acids.<sup>15</sup> Zinc oxide and para toner may be incorporated to form a coating composition.

Bradley<sup>16</sup> heated a mixture containing 100 parts of glycerol, 160 parts of phthalic anhydride and 110 parts of linseed oil fatty acids at 230-250°C. for about an hour, or until a sample on cooling was non-sticky. A stream of carbon dioxide or nitrogen was passed through during the heating. The resin after cooling was thinned with solvent naphtha to a 40 per cent solution. The addition of 1 per cent liquid cobalt drier to this solution results in the formation of a light-colored, quick-drying varnish. When the film is baked a wrinkled finish is obtained. Linseed oil fatty acids which have been distilled under reduced pressure yield a light-

<sup>10</sup> G. D. Patterson and R. A. Shive, U. S. P. 1,984,153, Dec. 11, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 854. E. I. du Pont de Nemours & Co., British P. 374,876, 1931, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.* B, 1932, 608. Canadian P. 315,437, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 1812. See W. W. Lewers and G. D. Patterson, U. S. P. 1,835,024, Oct. 25, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1215. Canadian P. 242,258, 1934, to Canadian Industries, Ltd.; *Chem. Abs.*, 1934, 28, 5691.

<sup>11</sup> E. S. Dawson, Jr., U. S. P. 1,803,174, Apr. 28, 1931, to General Electric Co.; *Chem. Abs.*, 1931, 25, 3855. British P. 252,394, 1925, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1927, 21, 2390. French P. 718,453, 1931, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 3126. German P. 547,969, 1933, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1932, 26, 3667. Canadian P. 292,353, 1929, to Canadian General Electric Co., Ltd.

<sup>12</sup> J. Scheiber, British P. 319,218, 1928, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1930, 24, 2623. German P. 565,180, 1929, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1933, 27, 1217.

<sup>13</sup> H. H. Hopkins and F. A. McDermott, U. S. P. 1,974,472, Sept. 25, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 7654. British P. 320,041, 1928; *Chem. Abs.*, 1930, 24, 2624. French P. 652,119, 1928; *Chem. Abs.*, 1929, 23, 3589.

<sup>14</sup> H. H. Hopkins, U. S. P. 1,950,363, May 22, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 4564. British P. 317,375, 1928; *Chem. Abs.*, 1930, 24, 2316. Canadian P. 310,124, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1931, 25, 3154.

<sup>15</sup> H. H. Hopkins, U. S. P. 1,950,320, May 22, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 4564. Canadian P. 331,450, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 3836.

<sup>16</sup> T. F. Bradley, U. S. P. 1,899,611, Jan. 10, 1932, to American Cyanamid Co.; *Chem. Abs.*, 1933, 27, 2318.

colored resin with glycerol and phthalic anhydride especially if the reaction is carried out in the presence of carbon dioxide.<sup>17</sup>

The solubility of linseed oil fatty acid resins in hydrocarbons increases in proportion to the amount of fatty acid. The resin made from 2 parts (by weight) of phthalic anhydride and 1 part of glycerol in the main is soluble only in alcoholic and ketonic solvents. If to this resin are added (A) 1 part, (B) 2 parts or (C) 4 or more parts of linseed oil fatty acids, the solubility in hydrocarbons progressively increases. (A) is partially soluble in coal-tar hydrocarbons and soluble in alcoholic toluene; (B) is soluble in coal-tar hydrocarbons; and (C) is soluble in petroleum hydrocarbons. The same solubility relationship holds when all the ingredients are heated simultaneously. Amieva<sup>18</sup> reported that resins containing enough linseed oil fatty acids to render them soluble in petroleum hydrocarbons dry faster when made by a modified two-stage process. He heated a mixture containing 2 parts of phthalic anhydride, 2 parts of glycerol and 4 parts of linseed oil fatty acids at about 200°C. for 6 hours and then added 2 parts more of phthalic anhydride. After heating for 6 hours longer the rubbery resin is easily soluble in petroleum hydrocarbons to give a solution which, with the addition of a small amount of liquid driers, forms a hard tough film in from 4 to 6 hours.

A higher temperature and a correspondingly shorter heating can also be used. Hopkins<sup>19</sup> heated a mixture of 171 parts of glycerol, 248 parts of phthalic anhydride, 490 parts of linseed oil acids and 164 parts of tung oil acids at 300°C. for 2 hours. The soft and sticky mass thus obtained can be mixed with ground cork and pigments and sheeted on a burlap backing to form a floor covering. Drying of the composition is carried out for several days at a temperature of about 100°C.

When raw tung oil is exposed to light in the presence of a trace of iodine or of sulphur, a solid modification, known as the  $\beta$ -form, is obtained.<sup>20</sup> Treatment with acetone and centrifuging eliminates the catalyst and the liquid oily residue. Saponification of the oily solid glyceride and neutralization yields the free  $\beta$ -eleostearic acid that can be heated with glycerol and phthalic anhydride to form a resin which dries faster than those containing the acids of other drying oils.<sup>21</sup>

When the acids of ordinary raw drying oils are used, the resin film is apt to be soft during the initial drying period but more brittle when completely dried. Pieper<sup>22</sup> sought to overcome this by substituting an oxidized fatty acid which tends to reduce the hardening effect of aging. That is, brittleness through oxidation of the film does not occur, since the drying oil acid is already more or less completely oxidized before it is combined. He heated a drying oil acid at 60-82°C. and passed air through it for 8 to 16 hours, or until it had become thoroughly oxidized. By heating 125 parts of the solid acid with the resin made from 50

<sup>17</sup> H. A. Hampton, British P. 408,667, 1932, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 5693. For the use of polymerized drying oil acids from which the volatile unpolymerized constituents have been removed by distillation, see R. Hill and E. E. Walker, British P. 428,864, 1933; to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.*, B, 1935, 683.

<sup>18</sup> M. A. Amieva, Jr., U. S. P. 1,875,498, Sept. 6, 1932, to W. P. Fuller & Co.; *Chem. Abs.*, 1933, 27, 200.

<sup>19</sup> H. H. Hopkins, U. S. P. 1,912,200, May 30, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 4100. British P. 354,324, 1930, to Imperial Chem. Ind., Ltd., and to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 5440. Canadian P. 308,107, 1931, to Canadian Industries, Ltd.

<sup>20</sup> A. W. Thomas and J. C. Thomson (*J.A.C.S.*, 1934, 56, 898) have recently given an improved method for the isolation of the  $\alpha$ - and  $\beta$ -eleostearic acids. A spectroscopic study of the eleostearic acids by A. Dingwell and J. C. Thomson (*J.A.C.S.*, 1934, 56, 890) has shown that the absorption bands of the  $\alpha$ - and  $\beta$ -eleostearic acids are very similar yet differences appear which enable the acids to be readily identified by this means. Even though light does have a profound effect on the acids, no difficulty was experienced in identification by this procedure. A stronger light source, however, produced a decided change in the structure of the  $\alpha$ -eleostearic acid.

<sup>21</sup> C. G. Gaucike, U. S. P. 1,920,980, Aug. 8, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5204. Canadian P. 330,337; *Chem. Abs.*, 1933, 27, 3351. French P. 678,539, 1929; *Chem. Abs.*, 1930, 24, 8662. British P. 341,012, 1929; *Chem. Abs.*, 1931, 25, 4137.

<sup>22</sup> E. J. Pieper, U. S. P. 1,845,330, Feb. 16, 1933, to Armstrong Cork Co.; *Chem. Abs.*, 1932, 26, 2334. British P. 363,345, 1930; *Brit. Chem. Abs.*, B, 1932, 272.

parts glycerol and 80 parts phthalic anhydride, immediate solution occurs, and the temperature is taken to 200°C. where it is held until the product has the right consistency. This resin is soluble and forms permanently flexible films.

Burke and Hopkins<sup>22</sup> used pentaerythritol instead of glycerol as the polyhydric alcohol. One formula includes 0.75 mol pentaerythritol, 1 mol phthalic anhydride and 1 mol linseed oil acids, the mixture being heated between 180° and 265°C. until foaming has ceased. Pentaerythritol resins dry more rapidly than those containing glycerol and form harder and more print-resistant films. Sorbitol,<sup>23</sup> or a mixture of sorbitol and a lower polyhydric alcohol, has also been suggested. The resin obtained from tung oil fatty acids can be hardened by heating with sulphur and the rubber-like mass thus formed may be mixed with waxes to form a floor-waxing composition. Quebrachitol has also been condensed with fatty acids of drying oils.<sup>24</sup>

The drying oil resins containing glycerol are fast-drying but the dried films are somewhat sensitive to washing with alkalis. Pieper<sup>25</sup> asserted that higher alkali-resistance is obtained when glycols are used with glycerol. This can be accounted for possibly by a higher degree of esterification with glycols in comparison with glycerol. Pieper mixed 35 parts of ethylene glycol, 3.5 to 7.5 parts of diethylene glycol, 8 to 13 parts of glycerol, 105 parts of phthalic anhydride and 10 to 20 parts of drying oil acids and heated the mass to about 220°C., just under the point of gelation. This formula utilizes only enough drying oil component to make the film flexible without imparting tackiness. The resin is soluble in the usual hydrocarbon, ester and glycol ether solvents and may be air-dried to form a film which can be washed with mild alkalis. Sherburne<sup>26a</sup> also used a mixture of glycol and glycerol. A resin was made by first heating 294 parts phthalic anhydride, 31 parts ethylene glycol, 59 parts succinic acid and 72 parts linseed oil fatty acids at 180-190°C. for 30 minutes and subsequently adding 127 parts glycerol and heating until the gel time at 200°C. by hot-plate test was 30-40 seconds. The resin becomes brittle on prolonged baking but is flexible and oil-resistant when baked for ½ hour at 100°C. Recommended uses are as a leather impregnant and as a coating for rubber and cloth.

The resin made by heating 1 mol each of phthalic anhydride, linoleic acid and glycerol can be treated with 5 per cent of sulphur chloride at 160°C. to give a product whose solutions are somewhat more viscous than those of the unsulphured resin and which dry more rapidly to films resistant to washing with sodium carbonate solutions.<sup>27</sup>

Bruson,<sup>28</sup> as stated, has used benzophenone-2,4'-dicarboxylic acid instead of phthalic anhydride for making drying oil resins. The principal advantages of this acid over phthalic anhydride are stated to be that it does not sublime during the heating operation, it has a higher melting point, it produces resins which do not soften as easily when warmed and the resin films show less solvent retention and therefore appear to dry faster. Bruson made a benzene-soluble resin by heating, for 4 hours at 250°C., a mixture of 135 g. benzophenone-2,4'-dicarboxylic

<sup>22</sup> C. E. Burke and H. H. Hopkins, U. S. P. 1,667,189, Apr. 24, 1928, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1928, 22, 2071. British P. 289,794, 1927, to Nobel Industries, Ltd.; *Chem. Abs.*, 1929, 23, 1002. Canadian P. 383,398, 1930, to Canadian Industries, Ltd.

<sup>23</sup> British P. 340,902, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5310. French P. 703,792; *Chem. Abs.*, 1931, 25, 4726.

<sup>24</sup> A. Hill and E. E. Walker, British P. 406,738, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 4923.

<sup>25</sup> E. J. Pieper, U. S. P. 1,847,783, Mar. 1, 1932, to Armstrong Cork Co.; *Chem. Abs.*, 1932, 26, 2881. British P. 360,990, 1930; *Brit. Chem. Abs. B.*, 1932, 235. Canadian P. 321,592, 1932; *Chem. Abs.*, 1932, 26, 2881.

<sup>26a</sup> A. J. Sherburne, Canadian P. 347,680, 1935, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1935, 29, 8072.

<sup>26b</sup> British P. 335,604, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3531. German P. 536,503.

<sup>28</sup> H. A. Bruson, U. S. P. 1,807,503, May 26, 1931, to Röhm & Haas Co., Inc.; *Chem. Abs.*, 1931, 25, 4159.

acid, 46 g. glycerol and 149 g. linseed oil fatty acids. Both isophthalic acid (benzene-m-dicarboxylic acid) and terephthalic acid (benzene-p-dicarboxylic acid) react with glycerol and linseed oil acids.<sup>29</sup> Rosenblum<sup>30</sup> replaced part of the phthalic anhydride by maleic acid and obtained light-colored resins from glycerol and drying oil acids.

Rubberseed oil, which by itself has a high acid value and poor drying properties, may be hydrolyzed and its hydrolytic products when incorporated in an alkyd resin give a cheap resin base which yields a tough film.<sup>30</sup> Rubberseed oil itself may be admixed,<sup>31</sup> as in the use of 6.75 parts of phthalic anhydride, 4.3 parts of 95 per cent glycerol, 2.55 parts of rubberseed oil and 3.2 parts of rubberseed oil acids, which are first heated at 175°C. and then finally at a temperature of 250°C. but avoiding gelation. The products are soluble in hydrocarbons, alcohols and esters.

#### USE OF DRYING OILS

Drying oils cannot be blended with phthalic glyceride by merely mixing in a common solvent, or by adding the oil to the fused resin. When a drying oil is heated with a mixture of phthalic anhydride and glycerol, combination of the oil occurs so slowly that the phthalic glyceride usually gels before all the oil has reacted. If glycol is used instead of glycerol a homogeneous resin is readily formed but its siccative properties are poor. To use drying oils and glycerol, the reaction is best carried out in the presence of a high-boiling liquid or by heating in an autoclave at a high temperature. However, glycerol may be first modified and the resin obtained by heating the drying oil with phthalic anhydride and the chemically modified glycerol.

Weber<sup>32</sup> heated a mixture of 94 parts of glycerol, 160 parts of phthalic anhydride and 80 parts of tung oil at a temperature of 235°C. in a vessel fitted with a short air-condenser. The product was a dark-yellow, hard and brittle resin containing a small amount of free oil. It had a softening point of 73°C. and an acid number of 56. This resin was soluble in a mixture of butyl acetate and butyl alcohol and was compatible with nitrocellulose in all proportions.

Combination of a drying oil with phthalic glyceride in any proportion can be accomplished by heating the two in the presence of a high-boiling solvent (benzyl benzoate, benzyl acetate, nitrobenzene, toluidine, benzyl alcohol, cresol, aniline, glycol diacetate, phenylhydrazine or o-cresyl benzoate). For example, when tung oil is added to a solution of phthalic glyceride in benzyl benzoate and heated for a long time at 200°C., the oil gradually thickens and finally disperses in the resin. Upon removal of the solvent by distillation, a sticky, viscous mass (a product of the resin and drying oil) is obtained.<sup>33</sup>

Monohydric alcohols also help to unite drying oils with glycerol and phthalic anhydride. The reaction can be carried out in the presence of a hydrocarbon or ester solvent, although the reaction occurs more rapidly if an excess of the alcohol is used. Glycerol, phthalic anhydride, tung oil and an alcoholic solvent (butyl alcohol, cyclohexanol) or glycol ethers or ethyl lactate are heated for about 20 hours

<sup>29</sup> See British P. 414,665, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 525.

<sup>30</sup> I. Rosenblum, U. S. P. 2,004,880, June 11, 1935; *Chem. Abs.*, 1935, 29, 5201.

<sup>31</sup> C. G. Moore and M. Zucker, U. S. P. 1,812,639, June 30, 1931, to Glidden Co.; *Chem. Abs.*, 1931, 25, 5049.

<sup>32</sup> C. G. Moore and E. H. Drake, U. S. P. 1,922,743, Aug. 15, 1933, to Glidden Co.; *Chem. Abs.*, 1933, 27, 5204.

<sup>33</sup> H. M. Weber, U. S. P. 1,690,515, Nov. 6, 1928, to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 512.

<sup>34</sup> L. V. Adams, U. S. P. 1,893,874, Jan. 10, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 2320. British P. 335,595, 1924, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1926, 20, 997. Canadian P. 262,979, 1926, to Canadian General Electric Co.; *Chem. Abs.*, 1926, 20, 3580.

under a reflux condenser. The resin solution thus formed can be used as a varnish.<sup>34</sup>

If glycerol is first chemically modified, as by forming a monobasic acid mono-glyceride, a drying oil reacts readily with the modified glycerol and phthalic anhydride to yield a resin. The increased reactivity of the oil is possibly to be ascribed to the fact that a monoglyceride can be considered a glycol which retards gelatinization and allows the oil time to combine. Moreover, the monoglyceride is more soluble in the oil than glycerol and the reaction occurs in the liquid phase rather than at the interface between the oil and phthalic glyceride. Morgan and Drummond<sup>35</sup> heated phthalic anhydride, tung oil and glycerol monobenzoate at 220-230°C.  $\alpha$ -Chlorohydrin can be substituted. The reaction product of glycerol with formaldehyde,<sup>36</sup> when heated with phthalic anhydride and tung or linseed oil is stated to yield a homogeneous resin. Varnishes prepared from such products dry rapidly in the air after the addition of cobalt linoleate. Linseed oil is more easily incorporated than tung oil.

Adams<sup>37</sup> effected combination of a drying oil with polybasic acid-polyhydric alcohol resins by heating them together in an autoclave until dispersion was complete. Since no loss of volatile matter can take place, combination of the oil and resin occurs by re-esterification and the formation of a mixed glyceride. A solvent may be added to the initial mixture, and instead of phthalic glyceride, the separate ingredients glycerol and phthalic anhydride can be used. The mixture is heated in the autoclave at temperatures between 190° and 230°C. for about 5 hours. The product can be dissolved and used as a baking varnish but does not air-dry; it can be made to do so satisfactorily by heating with a small amount of glycerol. Kienle<sup>38</sup> added 5 per cent of glycerol to the drying oil resin formed by autoclaving a mixture of 70 parts phthalic glyceride and 30 parts of linseed oil for 5 hours at 220°C. This product is heated in an open vessel at 240-260°C. until a drop, placed on a hot-plate at 200°C., gels in about 2 minutes, after which it is thinned with a mixture of toluene and solvent naphtha. This varnish dries tack-free in about 15 hours.

A two-stage process<sup>39</sup> has been used to overcome the risk of gelation which may occur with short-oil resins, that is, those resins in which there is less oil than resin. Thirty-one parts of glycerol, 74 parts of phthalic anhydride and 45 parts of bleached menhaden oil are heated in an enamelled autoclave for 4 hours at 240°C.; the heating is then continued at 193°C. in an open vessel and the water of esterification is driven off.

Bradley<sup>40</sup> first makes up what he terms a "synthetic flux" consisting of the reaction product of diethylene glycol, phthalic anhydride and tung (or linseed) oil and then heats this flux with glycerol and phthalic anhydride until the whole mass is homogeneous.

Baird, Hill and Walker<sup>41</sup> heated a resin made from glycerol, phthalic anhydride

<sup>34</sup> H. H. Morgan, A. A. Drummond and G. C. Attfield, British P. 327,946, 1928, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.* B, 1930, 677. German P. 608,368, 1935; *Chem. Abs.*, 1935, 29, 2623.

<sup>35</sup> H. H. Morgan and A. A. Drummond, British P. 329,335, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 5517. Austrian P. 23,292, 1929; *Chem. Zentr.*, 1930, 2, 2960. French P. 682,290, 1930.

<sup>36</sup> R. Hill, U. S. P. 2,505,499, June 18, 1935, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 8201. British P. 336,693, 1929; *Chem. Abs.*, 1931, 25, 2012.

<sup>37</sup> L. V. Adams, U. S. P. 1,893,874, Jan. 10, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 2330. British P. 273,399, 1926, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1928, 22, 1863. French P. 638,275, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 293.

<sup>38</sup> R. H. Kienle, U. S. P. 1,885,840, Feb. 21, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 2592. British P. 364,242, 1931, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B, 1933, 156. French P. 718,453, 1931, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 8126.

<sup>39</sup> W. Baird, British P. 350,173, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 616.

<sup>40</sup> T. F. Bradley, U. S. P. 1,953,412, Mar. 27, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 3606. <sup>41</sup> W. Baird, R. Hill and E. E. Walker, British P. 328,008, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 5173. French P. 687,894, 1930; *Chem. Abs.*, 1931, 25, 835.

and oleic acid and added linseed oil slowly to the melt. A clear product is obtained after heating for about 2 hours at 230°C. The resin from linseed oil acids, phthalic anhydride and glycerol can be combined with linseed oil in the same way. Baird and Walker<sup>42</sup> have extended this method to first incorporating glycerol, phthalic anhydride and castor oil by heat and then adding with further heat a non-hydroxylated oil such as tung or linseed.

Castor oil is a non-drying oil. It is hydroxylated and differs from other vegetable oils in its ease of incorporation into alkyd resins.<sup>43</sup> A homogeneous product for varnishes is made by the destructive distillation of castor oil<sup>44</sup> until the residue is from 60-80 per cent of its original weight. The residue is esterified with glycerol and condensed with phthalic anhydride.<sup>45</sup> Heating the castor oil under reduced pressure yields lighter-colored products. The same method has been applied to mixtures of castor oil and vegetable drying oils having an iodine value above 100.<sup>46</sup>

Heck<sup>47</sup> vacuum-distilled castor oil at a pressure of 30 mm. and at a temperature of 260-270°C. and obtained essentially 9,11-octadecadiene-1-acid. This acid is heated with glycerol and phthalic anhydride at 180-230°C. until a resin is obtained which is non-tacky and soluble in benzene, toluene and coal-tar oils.

Modified polyhydric alcohol-polybasic acid resins containing a sufficient amount (usually over 50 per cent) of monobasic acid are miscible with drying oils and the resin-oil solution can be condensed by further heating. This allows the preparation of resins containing an increased amount of siccative component.

Adams<sup>48</sup> incorporated more drying oil in a finished resin to make a more flexible and adhesive cementing composition. A linseed-phthalic glyceride resin is heated until a test sample hardens in 1.5 minutes at 200°C., whereupon a small amount of bodied linseed oil is added and the mixture heated until it is homogeneous.

#### USE OF SOLUTIONS OF DRYING OILS IN POLYBASIC ACIDS

Another method of incorporating a drying oil with phthalic glyceride consists in first preparing a solution of the oil in phthalic anhydride by heating them together. If glycerol is now slowly added it dissolves and reacts readily since the polybasic acid, being in excess, acts as a blending agent. The composite resin, formed in the mixture as glycerol is added, is also a blending agent and allows a homogeneous product to be formed. Dawson<sup>49</sup> dissolved 70 parts of linseed oil by mixing with 206 parts of molten phthalic anhydride. About 92 parts of glycerol were added to the solution and the mixture heated gradually to about 250°C. A brownish resin is obtained whose solutions form a varnish which can be dried at ordinary temperatures or baked. It can also be used in a limited way as a mold-

<sup>42</sup> W. Baird and E. E. Walker, U. S. P. 1,925,947, Sept. 5, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 5562.

<sup>43</sup> See Chapter 43.

<sup>44</sup> E. C. Holton, U. S. P. 1,799,420, April 7, 1931, to Sherwin-Williams Co.; *Chem. Abs.*, 1931, 25, 3184.

<sup>45</sup> For the use of this resin with nitrocellulose, see C. T. Ellis, U. S. P. 1,934,261, Nov. 7, 1933, to Sherwin-Williams Co.; *Brit. Chem. Abs. B*, 1934, 805.

<sup>46</sup> E. C. Holton, U. S. P. 1,888,595, Nov. 22, 1932, to Sherwin-Williams Co.; *Chem. Abs.*, 1933, 27, 1528. Canadian P. 348,347, 1935; *Chem. Abs.*, 1935, 29, 3538.

<sup>47</sup> A. Heck, U. S. P. 1,947,416, Feb. 13, 1934, to Cook Paint & Varnish Co.; *Chem. Abs.*, 1934, 28, 2556. See Chapter 43.

<sup>48</sup> L. V. Adams, U. S. P. 1,900,537, Mar. 7, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 3045. British P. 353,713, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1932, 26, 3633. French P. 699,765, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 3503. German P. 598,736, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 5941.

<sup>49</sup> E. S. Dawson, Jr., U. S. P. 1,888,849, Nov. 22, 1932, to General Electric Co.; *Chem. Abs.*, 1933, 27, 1530. British P. 285,459, 1928, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1928, 720. French P. 35,164, 1928, addn. to 638,275, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1930, 24, 2317. German P. 578,707, 1933, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 920. Canadian P. 292,355, 1929, to Canadian General Electric Co., Ltd.

ing material since it is converted to the infusible state by heating at about 200°C. for an hour under a pressure of 1000 pounds per square inch.

Schlingman<sup>80</sup> observed that there is always a slight amount of water present in a drying oil and when the oil is heated an equilibrium is set up as follows:

Drying oil + water  $\rightleftharpoons$  glycerol + drying oil acids. This equilibrium is such that the amounts of glycerol and oil acids are small. In the presence of an acid such as phthalic anhydride, however, the equilibrium is disturbed on account of reaction of this acid with the glycerol formed by hydrolysis of the oil, yielding phthalic glyceride and liberating water. The water thus formed is the same in amount as originally present and it again hydrolyzes more oil to yield again more glycerol and drying oil acids in a continuing cycle. When the reaction is carried out under reflux conditions so that the water is retained in the system the mixture that finally results consists of phthalic glyceride, drying oil acids, water and any excess of phthalic anhydride (as acid) that was used. If glycerol is now added the excess acid is combined and a homogeneous resin is obtained. Schlingman carried out this process as follows: 243 g. phthalic anhydride are heated to about 270°C. in a container provided with a reflux condenser and 200 g. linseed oil are slowly added drop by drop, maintaining the temperature between 270° and 300°C. during the operation. After all the oil has been introduced, 100 g. glycerol are slowly added to the mass. The resinous product is usually formed by the time all the glycerol is in, and the final heating may be done in an open vessel to allow the escape of water. This resin contains 36.8 per cent of combined oil, but a resin containing other proportions may be made in the same manner.

#### USE OF DRYING OIL MONOGLYCERIDES

As indicated, the monoglycerides of the fatty acids of drying oils combine readily with polybasic acids to form drying oil resins. The monoglycerides may be made in several ways: (1) by heating 1 mol of the free acid with 1 mol of glycerol; (2) by heating the drying oil itself (a triglyceride) with glycerol until re-esterification occurs between the oil and glycerol or (3) enzymatic partial hydrolysis. In no case is the product a pure monoglyceride but contains some diglyceride, triglyceride and perhaps a little free glycerol. The second process of forming monoglycerides is one of alcoholysis and is accelerated by use of catalysts.<sup>81</sup>

Kienle<sup>82</sup> prepared the monoglyceride of linseed oil acids by heating the acids with a large excess of glycerol. Linseed oil can be mixed with the monoglyceride thus obtained and the subsequent addition of phthalic anhydride to the hot solution yields a drying oil resin. About 100 g. linseed fatty acids and 92 g. glycerol are heated at 200-250°C. until combination has occurred and 392 g. linseed oil are stirred in, followed by 200 g. phthalic anhydride. Heating is continued until a test drop, placed on a hot plate at about 200°C., hardens in less than 5 minutes. The drying oil can be added all at once as above, or part of the oil can be mixed with the monoglyceride and the rest added after phthalic anhydride has been introduced. Hence it is possible to incorporate practically any proportion of oil desired.

<sup>80</sup> P. F. Schlingman, U. S. P. 1,898,790, Feb. 21, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 2631. British P. 370,440, 1930, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1932, 614. French P. 707,159, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 611. Canadian P. 321,622, 1932, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1932, 26, 3993. German P. 691,479, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 2556.

<sup>81</sup> Mono- and diglycerides may be prepared in the presence of an alcoholate catalyst mixture of glycerol, triglyceride and alkali metal alcoholate at 170-205°C. Soap can also be used. See A. Edeler and A. S. Richardson, Canadian P. 340,803, 340,804 and 340,805, 1934, to Procter & Gamble Co.; *Chem. Abs.*, 1934, 28, 4340. British P. 421,063, 1933; *Brit. Chem. Abs. B*, 1935, 189.

<sup>82</sup> R. E. Kienle, U. S. P. 1,889,923, Dec. 6, 1932, to General Electric Co.; *Chem. Abs.*, 1933, 27, 1774. British P. 318,319, 1923, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1930, 24, 1758. French P. 27,324, 1929, adds to 654,175, 1928, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 3383. Belgian P. 343,571, 1930, to Société d'Electricité et de Mécanique.



Soluble balsam-like products that dry readily in the presence of metallic driers to give flexible films are obtained from linoleic monoglyceride (monolinolein) and diglycolic acid or anhydride. Thus, 180 parts of linoleic monoglyceride and 55 parts of diglycolic anhydride are heated for 8 hours at 120-125°C.; the temperature is then raised to 160°C., and the mixture heated 8 hours longer until the acid number is about 20.<sup>55</sup>

Ott, Frick and Bernard<sup>54</sup> heated 282 parts by weight of linseed oil and 92 parts of glycefol for 3 hours at 170-180°C. in an atmosphere of carbon dioxide and then gradually increased the temperature to 230°C. After adding 148 parts of phthalic anhydride the mixture was heated 3 hours longer at 230°C. The product was a viscous, light-brown resin readily soluble in drying and non-drying oils.<sup>55</sup> In another case, 0.05 part of calcium glycerate was added to 872 parts of linseed oil and 276 parts of glycerol; the mixture was heated for 2 hours at 250-280°C., 518 parts of phthalic anhydride were introduced, and finally the temperature was raised gradually to 300°C. for an hour. The acid number of the resin thus formed was reduced to 10 by allowing a stream of nitrogen to pass through it as it cooled. The resin was a clear, pale yellow material, readily soluble in aromatic hydrocarbons, esters and ketones. When this resin is heated with about 3 per cent of sulphur, or with about 5 per cent of sulphur chloride at temperatures below 200°C. the product is soluble and forms films which are tougher, dry faster and have better adhesion than the untreated resin. Using amounts of sulphur greater than 5 per cent yields insoluble products.<sup>56</sup>

Boiled drying oils can be heated with glycerol first to facilitate their combination in a resin.<sup>57</sup> Kienle<sup>58</sup> used a boiled linseed oil obtained by heating the oil at 300°C. until it had reached the desired body. Forty parts by weight of this oil and 20 parts of glycerol are mixed and heated at about 250°C. until the originally turbid mixture becomes clear. Then 49 parts of phthalic anhydride are added and the temperature held at 235°C. until the whole melt is again homogeneous. Tung oil can be combined in a resin by this process. For example, 400 parts of tung oil are heated to 235°C., 100 parts glycerol are added gradually and the mixture is heated until clear. The addition of 243 parts of phthalic anhydride forms a tung oil resin. Lighter-colored resins which do not yellow on aging are made by this process if the oil is first bleached (by heating it to 260-290°C. in the absence of oxygen).<sup>59</sup> The linseed oil is heat-treated at 270°C. and a rapid current of carbon dioxide is bubbled through the oil for 5 hours. The viscosity of the oil increases whereas the color diminishes. The oil is cooled to 250°C., glycerol poured in and the mass agitated for 3.5 hours. Molten phthalic anhydride is added and carbon dioxide bubbled through the reactants during esterification. On the other hand, tung oil can be heated with glycerol and the partially esterified

<sup>55</sup> French P. 677,428, 1929, to I. G. Farbenind. A.-G.

<sup>54</sup> K. Ott, F. Frick and H. Bernard, German P. 547,517, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3686. British P. 216,914, 1928; *Chem. Abs.*, 1930, 24, 1997. French P. 660,671, 1928; *Chem. Abs.*, 1930, 24, 253. See F. Frick, German P. 585,353, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1485.

<sup>56</sup> E. Münch and G. Kraemer (German P. 587,037, 1933, addn. to 547,517, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2555) treat linseed oil with ethylene oxide before condensing with phthalic anhydride.

<sup>57</sup> British P. 338,604, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2531.

<sup>58</sup> Boric acid heated with linseed oil causes polymerization but retards gelation. See R. E. Coleman, British P. 413,162, 1933, to British Thomson-Houston Co.; *Chem. Abs.*, 1935, 29, 626.

<sup>59</sup> R. H. Kienle, British P. 356,340, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1932, 26, 5778. French P. 39,011, 1930, addn. to 638,275, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 1811.

<sup>60</sup> J. W. Iliff and P. Robinson, U. S. P. 1,972,521, Sept. 4, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 6587. British P. 359,355, 1930; *Chem. Abs.*, 1932, 26, 4970. Canadian P. 322,657, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 3045. See also J. W. Iliff and P. Robinson, U. S. P. 1,886,630, Jan. 8, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 29, 1663. See British P. 377,265, 1933, to Deutsche Gasföhrlieht-Auer-G.m.b.H.; *Chem. Abs.*, 1933, 27, 4111, for treating olive and linseed oils with ozone or potassium permanganate.

alcohol is heated with linseed oil fatty acids. The mixed acid ester is then re-alcoholized and further esterified with phthalic anhydride.<sup>60</sup> Moore<sup>60a</sup> used a small amount of sodium hydroxide as a catalyst in forming the monoglyceride from a mixture of tung or rubber-seed oil and glycerol.

Bradley<sup>61</sup> added to the drying oil alkyds a small amount of oil-soluble phenols in order to prevent frosting. Glycerol, phthalic anhydride, tung oil fatty acids, tung oil and linseed oil fatty acids were heated to 240°C. To the hot mixture were added o-hydroxybiphenyl and tung oil which had been pre-heated to 290°C. The mixed resin, thinned with turpentine, yields a varnish which does not frost in an impure atmosphere such as is found in gas-fired baking ovens.

Instead of heating the drying oil with a polyhydric alcohol, Baird and Hill<sup>62</sup> heated it with the product formed from phthalic anhydride and an excess of glycerol. After the oil and hydroxyl-containing intermediate have combined, sufficient polybasic acid is introduced to unite with the free hydroxyl groups.

By avoiding heat and alkali in hydrolysis, both polymerization and discoloration of the oil are inhibited. Robinson<sup>63</sup> used an enzyme preparation to bring this about. The enzyme is essentially lipase and is prepared from castor beans which have been allowed to remain at 25°C. for several days to promote germination and then crushed with sand in the presence of 0.5 per cent toluene. By allowing 8 parts of the enzyme in 200 parts of water of pH 5 (buffered with phosphates) and 200 parts of alkali-refined linseed oil to stand for 30 days at 25°C. an oily layer is formed of acid number of 73. Tung oil is also partly hydrolyzed by this procedure; after 75 days, the acid number is 61. By heating to 250°C., 206 parts of the filtered partially hydrolyzed oil, 96 parts of phthalic anhydride and 42 parts of glycerol, a clear, not excessively dark resin is obtained of decidedly superior drying qualities.

#### MIXTURES OF DRYING OILS AND THEIR FATTY ACIDS

As previously mentioned, the drying oil acids are fairly easy to incorporate into a polyhydric alcohol-polybasic acid resin but the free oils (glycerides) are relatively difficult to use and call for the various modifications of procedure already noted. If the oil is mixed with some of its own fatty acids, however, combination is easier since the latter act as a blending agent. The mixtures of oil and fatty acids may include simple blends or they may be partially hydrolyzed oils. Bradley<sup>64</sup> heated a mixture of 75 parts of glycerol, 148 parts of phthalic anhydride, 85 parts of linseed oil fatty acids and 85 parts of tung oil, at a temperature of 230-250°C. for an hour and thus made a clear resin whose solutions dry rapidly.<sup>65</sup>

Heating 135 parts of benzophenone-2,4'-dicarboxylic acid and 46 parts of glycerol with 120 parts of linseed oil fatty acids and 50 parts of linseed oil at 240°C. for 4 hours yields a clear, tough resin soluble in butyl acetate, toluene and acetone.<sup>66</sup>

<sup>60</sup> C. G. Gauker, U. S. P. 1,979,260, Nov. 6, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 267. British P. 405,827, 1934; *Chem. Abs.*, 1934, 28, 4924.

<sup>60a</sup> C. G. Moore, Canadian P. 545,945, 1935, to Glidden Co.; *Chem. Abs.*, 1935, 29, 3422.

<sup>61</sup> T. F. Bradley, British P. 407,965, 1934, to American Cyanamid Co.; *Chem. Abs.*, 1934, 28, 5692. For the use of dihydroxydiphenylmethanecarboxylic acid with rosin tung oil and glycerol, see O. A. Cherry, U. S. P. 1,933,733, Dec. 4, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1935, 29, 523. Cf. Chapters 17 and 19.

<sup>62</sup> W. Baird and R. Hill, British P. 304,737, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 1775.

<sup>63</sup> P. Robinson, U. S. P. 1,925,935, Sept. 5, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5592. Canadian P. 331,535, 1933, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 2837.

<sup>64</sup> T. F. Bradley, U. S. P. 1,893,611, Jan. 10, 1933, to American Cyanamid Co.; *Chem. Abs.*, 1933, 27, 2919. British P. 418,558, 1934; *Chem. Abs.*, 1934, 28, 7561.

<sup>65</sup> See W. Baird, R. Hill and E. E. Walker (British P. 323,003, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 8173. French P. 637,534, 1930; *Chem. Abs.*, 1931, 25, 835) discussed above.

<sup>66</sup> H. A. Bruen, U. S. P. 1,897,503, May 26, 1931, to Rohm & Haas Co., Inc.; *Chem. Abs.*, 1931, 25, 4194.

## USE OF NATURAL RESINS

All the drying oil resins thus far described in this chapter have been of the three-component type, polyhydric alcohol, polybasic acid and a drying oil residue. If rosin or another natural resin is used with these constituents, a harder and fairly durable resin is obtained. Rosin serves to cheapen the product and for ordinary purposes forms an acceptable additive. The addition of rosin makes incorporation of the drying oil component with the resin much easier. In the presence of sufficient rosin the fatty acids react very quickly and even glyceride oils can be combined with great ease, since it acts as a blending and fluxing agent. With sufficient drying oil (or drying oil acid) on the other hand, the alkyds will dissolve both the natural and the synthetic resins.<sup>67</sup> Tung oil and rosin with glycerol phthalate resin yields a water-resistant coating. By heating 101 parts of glycerol, 164 parts of phthalic anhydride, 140 parts of tung oil and 200 parts of rosin at 285-290°C. combination between the components is effected. Tung oil appears to combine at temperatures as low as 200-210°C.<sup>68</sup>

A resin may be made by heating 92 parts by weight of glycerol, 148 parts of phthalic anhydride, 142 parts of linseed oil acids and 175 parts of rosin at 220°C. until a test-sample is clear and tough. A stream of carbon dioxide passed through the melt during the heating produces a lighter color than when the reaction occurs in contact with air. If Congo copal is used instead of rosin, the resin is less brittle.<sup>69</sup>  $\beta$ -Eleostearic acid, glycerol, phthalic anhydride and Congo copal, heated gradually to 250°C., form a soluble resin whose solutions dry very rapidly on exposure.<sup>70</sup>

The use of a mixture of rosin and castor oil to modify a drying oil resin has been proposed by Durant.<sup>71</sup> He heated phthalic anhydride, glycerol and linseed oil acids with rosin and castor oil at 240-260°C. until the acid number of the product was below 25. This resin is convertible by further heating into an infusible, insoluble mass. The drying properties can be increased by heating with a mixture of linseed and tung oil. Durant and Strutchfield<sup>72</sup> have further incorporated dibasic aliphatic acids. Phthalic anhydride, glycerol, succinic acid, ethylene glycol, rosin and tung oil are heated to 250°C. The oil-modified alkyd is soluble in acetone, cellosolve, butyl carbitol, cellosolve acetate, ethyl acetate, furfural and toluene, and has a high dielectric value.

Burke and Hopkins<sup>73</sup> used a mixture consisting of 3 mols of pentaerythritol, 4 mols of phthalic anhydride, 2 mols of linseed oil acids and 2 mols of rosin. The ingredients are heated between 180-265°C. for 7-10 hours.

<sup>67</sup> H. A. Hampton and R. Hill, British P. 406,991, 1932, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1934, 413.

<sup>68</sup> Carleton Elms, U. S. P. 1,958,614, May 15, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 4615.

<sup>69</sup> H. H. Hopkins and F. A. McDermott, U. S. P. 1,974,472, Sept. 25, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 7564. British P. 320,041, 1928; *Chem. Abs.*, 1930, 24, 2624. French P. 652,119, 1928; *Chem. Abs.*, 1929, 23, 3589.

<sup>70</sup> C. G. Gauerke, U. S. P. 1,920,980, Aug. 8, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 5204. British P. 341,012, 1929; *Chem. Abs.*, 1931, 25, 4187. French P. 878,539, 1929; *Chem. Abs.*, 1930, 24, 3662. Canadian P. 330,887, 1929; *Chem. Abs.*, 1930, 24, 3662. See A. M. Collins, Canadian P. 324,734, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 5439.

<sup>71</sup> W. W. Durant, British P. 343,024, 1928, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1931, 25, 4423. French P. 37,670, 1929, addn. to 649,384, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 4724; 1929, 23, 2841. See Chapter 47.

<sup>72</sup> W. W. Durant and P. H. Strutchfield, U. S. P. 1,975,569, Oct. 2, 1934, to General Electric Co.; *Chem. Abs.*, 1934, 28, 7563. British P. 393,034, 1932, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1933, 640. Canadian P. 342,596, 1934, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1934, 28, 6008. German P. 603,931, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1935, 29, 857. French P. 41,896, addn. to 726,745, 1931, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 27, 4701.

<sup>73</sup> C. E. Burke and H. H. Hopkins, U. S. P. 1,667,189, Apr. 24, 1928, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1928, 22, 3071. British P. 289,794, 1927, to Nobel Industries, Ltd.; *Chem. Abs.*, 1929, 23, 1002. Canadian P. 353,996, 1930, to Canadian Industries, Ltd.

When  $\beta$ -eleostearin (obtained by the action of ultraviolet light on tung oil) is pre-heated to 500°F., it becomes soluble in high-boiling gasoline or naphtha. After heat-treatment it may be added directly to drying oils (linseed) to render them faster drying or it may be incorporated in an alkyd-resin glyceride by heat.<sup>74</sup> Another procedure for incorporating tung oil is as follows. Tung oil is first heated to 300°C. in the presence of zinc rosinate and to the heated oil is added a reaction product of glycerol, phthalic anhydride, linoleic acid and maleic acid.<sup>75</sup> By heating maleic anhydride with a dihydric alcohol and subsequently incorporating rosin a strongly acidic resin is formed. Further esterification with glycerol and drying oils and drying oil fatty acids yields a homogeneous resinous mass.<sup>76</sup>

Kienle<sup>77</sup> heated 390 parts by weight of tung oil to 280°C. and added 85 parts of glycerol gradually to the hot oil. As soon as the mixture was homogeneous he introduced 191 parts of phthalic anhydride and 120 parts of rosin and heated it further until all ingredients had combined. Schlingman<sup>78</sup> reversed the process by adding the drying oil to the heated mixture of rosin and phthalic anhydride. Then, 118 g. phthalic anhydride and 63 g. rosin are heated to 270°C. and a mixture of 92 g. linseed oil, 18 g. tung oil and 8 g. castor oil is added drop by drop. After the oils have been completely incorporated 56 g. glycerol are added and the entire mass further heated at 200°C. until clear. Baird<sup>79</sup> still further modified the process. He heated linseed (or blown linseed) oil and rosin with glycerol, in excess of the amount needed for the initial esterification, until the product was homogeneous; the excess was then neutralized with phthalic anhydride.

Drying oils can be mixed with a rosin-phthalic glyceride resin merely by adding the oil to the molten resin. If the initial resin contains sufficient rosin (about 50 per cent), solution occurs at once, but if the rosin content is lower, the mixture must be heated for a period to obtain a homogeneous product. If the oil is only dispersed in the rosin-phthalic glyceride and there is no chemical combination between the oil and the resin molecule, the drying oil alkyd solution or dispersion is more closely related to usual varnish bases. Warren, Newbound and Ward,<sup>80</sup> by heating a glycerol phthalate resin with a natural or synthetic resin for some hours, obtained a clear transparent product which readily dissolved in fatty oils under short heat treatment. The solution may be thinned to a varnish of the desired consistency by addition of acetone, turpentine or hydrocarbon solvents. In an example, 1 lb. of glycerol phthalate resin and 2 lb. of rosin are heated to 220° for 6 hours. The product may be dissolved in 2.5 lb. of linseed oil by heating to 320° for 2 minutes.

The glycerol-natural resin-phthalate modification with drying oils may be effected by heating equal weights of prepared resin and linseed oil or other drying oil in an autoclave to 210° for 6 hours, or until homogeneous.<sup>81</sup> The product is a

<sup>74</sup> C. G. Gauerke, U. S. P. 1,838,088, Feb. 21, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 2630. British P. 312,053, 1929; *Brit. Chem. Abs. B.*, 1930, 9371. Canadian P. 305,654, 1930; *Chem. Abs.*, 1931, 23, 534.

<sup>75</sup> I. Rosenblum, U. S. P. 1,972,905, Sept. 11, 1934; *Chem. Abs.*, 1934, 28, 6968.

<sup>76</sup> French P. 770,303, 1934, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1934, 28, 524.

<sup>77</sup> R. H. Kienle, British P. 356,340, 1930, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1932, 26, 9772. French P. 59,011, addn. to 538,378, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 1211.

<sup>78</sup> P. P. Schlingman, U. S. P. 1,898,700, Feb. 21, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 2631. British P. 370,445, 1930, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B.*, 1933, 614. French P. 707,184, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 26, 611. Canadian P. 331,523, 1933, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1933, 26, 5393.

<sup>79</sup> W. Baird, British P. 361,398, 1931, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 5304.

<sup>80</sup> H. W. H. Warren, R. Newbound and A. T. Ward, British P. 308,671, 1927, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 24, 516. French P. 36,364, 1925, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1926, 24, 4173.

<sup>81</sup> A. H. V. Durr, U. S. P. 1,739,447, Dec. 19, 1928, to Compagnie nationale du Nord réunies (Etablissements Kuhlmann); *Chem. Abs.*, 1930, 24, 393. U. S. Reissue 17,375, Nov. 25, 1930; *Chem. Abs.*, 1931, 25, 435. Compagnie nationale du Nord réunies (Etablissements Kuhlmann), British P. 303,387, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1928, 23, 6364.

viscous, yellow-green fluorescent mass which may be dissolved in naphtha or other hydrocarbon solvent on warming. The filtered solution forms a varnish which dries rapidly at a high temperature (3 minutes at 300°C., 15-20 hours at 110°C.) to a film which is both flexible and of a good dielectric strength. The varnishes are responsive to the customary siccative agents.

The use of natural resins, particularly the formerly despised rosin, as an aid in the commercial production of drying-oil alkyds has proved a great boon to the coating industry, as important in its way as the revolutionary discovery of the drying-oil alkyds themselves.

## Chapter 45

### Modified Alkyd Resins

#### III. Use of Other Synthetic Resins

The modification of alkyd resins by means of other synthetic resins, and particularly by the phenol-formaldehyde products, has yielded a considerable number of plastic materials for use in the production of varnishes, coating and molding compositions. Polyhydric alcohol-polybasic acid resins possess the desirable qualities of toughness, flexibility and ready solubility in numerous organic solvents, nevertheless they harden slowly under the action of heat. This property may be partially eliminated by the addition of drying oils and drying oil acids. Another alteration is by certain additions of phenol-formaldehyde resols. Moreover, the glycerol phthalate condensation products, due to their superior flexibility, can be made to compensate for the brittleness of some of the other synthetic resins. This applies again to the phenol-aldehyde type. In general, the solubility of the modified alkyd resins varies according to the type of synthetic resin modifier.

#### MODIFICATION BY PHENOL-FORMALDEHYDE RESINS

The incorporation of alkyd resins with phenol-formaldehyde resins<sup>1</sup> is capable of yielding plastics which in certain respects have better qualities than either component individually. Resins of the first type are superior in respect to mechanical strength, toughness and resistance to shock, whereas phenol-formaldehyde resins are harder and have less tendency to stick in molding. The latter may be molded quickly and be hardened or "cured" by a relatively short heat-treatment. By mixing in judicious proportions the two resins, products are obtained which possess good mechanical properties and which are said to be capable of being molded as readily as the phenol-aldehyde resins.<sup>2</sup> An early application of the mixed resins was made by Weisberg<sup>3</sup> who found that the proportions of the two resins could be varied widely, and that fillers or coloring matter (talc, rotten stone, wood flour, asbestos, iron oxide or chromium oxide) could be incorporated. A greater proportion of filler may be used than is possible when operating with phenol-formaldehyde resins alone. The two resins may be mixed by using a mutual solvent (acetone, alcohol or ethyl acetate),<sup>4</sup> a procedure which is said to be useful when the final product is to be employed as a varnish. When no fillers are added and when the resin is fusible, the two resins may be melted together. When one or both of the resins, however, are infusible, it is more advantageous to swell the resins together with the fillers by the use of hot acetone. In addition to the use in varnish manufacture, these resins are good electrical insulators.

<sup>1</sup> See Chapters 19 and 20.

<sup>2</sup> For the oil-reactive phenolic resin combinations with alkyds which require no stoving, see H. Urieh, *Farben-Ztg.*, 1934, 25, 1994; *Brit. Chem. Abs. B.*, 1934, 1069. See also W. Krumhaar, *Fed. Paint Varnish Prod. Club. Official Digest*, 1935, 142, 15.

<sup>3</sup> L. Weisberg, U. S. P. 1,449,965, Jan. 30, 1923; to Barrett Co.; *Chem. Abs.*, 1923, 17, 1341.

<sup>4</sup> H. E. Hopkins (Canadian P. 343,339, 1934; *Chem. Abs.*, 1934, 28, 7553) has used as a solvent for phenol-formaldehyde-alkyd resins a petroleum hydrocarbon of b.p. 60-260° and having an aniline point of -5 to 10° with a dielectric value of about 15 to 25.

Hönel<sup>6</sup> has extended the process of mixing alkyds with phenol-aldehyde resins so as to include a much wider range of starting materials. For example, the initial resin may be derived by heating at 160-170°C. 100 parts of phthalic anhydride and 63 parts glycerol until an acid number of 228 is attained. To the thus-formed glycerol phthalate monoester are added 60 parts of linseed oil fatty acids and 60 parts of American rosin M and the components melted. Further, a liquid reaction product obtained from 35 parts of technical m-p-cresol and 40 parts of formaldehyde (40 volume per cent) is then stirred into the mix at 160-180°C.; a homogeneous mass results. The temperature is raised to 200°C., 120 parts of linseed oil are added slowly and the mixture is heated at 280°C. for several hours. The product is soluble in aromatic or in mixtures of aliphatic and aromatic hydrocarbons and, when incorporated with driers, forms a hard varnish. The turbidity which appears in the reacting mass when an acid number of 30 is reached can be dispersed by the addition of a small amount of glycerol. Tung oil, or its fatty acids with a corresponding amount of glycerol, may be added simultaneously with the phenol-aldehyde resin. Moreover, castor oil may be substituted for linseed oil.

A further method of preparing a varnish resin of the above type is to condense 50 parts of maleic anhydride with 50 parts of glycerol at 160°C., until a clear oily product with an acid number of about 280 is obtained. Five hundred parts of American wood rosin and 150 parts of tung oil fatty acids are melted and combined with the first product. The liquid formed by the condensation of 120 parts of cresol and 160 parts of formaldehyde is then stirred in. When the reacting mass is uniform, 50 parts of tung oil, 550 parts of linseed oil and 60 parts of glycerol are added, and the entire mixture esterified. The resulting material serves as an excellent base for varnishes. A product soluble in petroleum hydrocarbons is derived from camphoric acid, glycerol, American or French rosin and corn oil fatty acids, together with the cresol-aldehyde condensate.<sup>6</sup>

The material obtained by reacting natural with phenol-aldehyde resins may be combined with a polyhydric alcohol and a carboxylic acid.<sup>7</sup> The phenol-aldehyde condensate may be derived from 150 parts of technical m-p-cresol and 180 parts of 40 per cent formaldehyde condensed by means of alkali and then introduced into 1000 parts of melted French rosin W G. The temperature of the melt is raised to 210°C. Further, 300 parts of benzoic acid and 200 parts of glycerol are added and the final esterification is carried out at 270°C. The resulting resin has a rather low melting point, but is tough and has good adhesive qualities. It is soluble in aromatic hydrocarbons and the usual mixed nitrocellulose solvents and is compatible with nitrocellulose in all proportions.

Butyric, succinic, maleic, adipic, phthalic, camphoric or citric acid may be used in place of benzoic acid. When the phenol used is substituted in the para positions (as, for example, by treating m-cresol with sulphuryl chloride), the resin finally obtained possesses a satisfactory light-proofness. A resin of the type described above may also be combined with fatty oils by heating to 240-280°C.; such materials tend to be more soluble in petroleum hydrocarbons.

In general, when an ester is heated with a low-molecular-weight resin obtained by alkaline condensation of formaldehyde with a phenol, products for coatings, impregnating agents and binders are formed.<sup>8</sup> The polyhydric alcohol esters of mono- or polybasic acids are especially used, and the reaction is carried out in absence of solvent or dispersing agent. For the condensation with formaldehyde the

<sup>6</sup> H. Hönel, U. S. P. 1,870,453, Aug. 9, 1932, to Beck, Koller & Co., Inc.; *Chem. Abs.*, 1932, 26, 5777.

<sup>7</sup> H. Hönel, U. S. P. 1,870,454, Aug. 9, 1932, to Beck, Koller & Co., Inc.; *Chem. Abs.*, 1932, 26, 5777.

<sup>8</sup> H. Hönel, U. S. P. 1,870,454, Aug. 9, 1932, to Beck, Koller & Co., Inc.; *Chem. Abs.*, 1932, 26, 5777. See also H. Hönel, U. S. P. 1,908,980, July 31, 1934; *Chem. Abs.*, 1934, 28, 5941.

<sup>9</sup> H. Hönel, U. S. P. 1,908,353, 1,908,354, 1,908,355 and 1,908,356, Jan. 15, 1935, to Beck, Koller & Co.; *Chem. Abs.*, 1935, 29, 1537. British P. 234,672, 1929; *Brit. Chem. Abs. B*, 1930, 1164. French P. 676,456, 1929; *Chem. Abs.*, 1930, 24, 8002. German P. 545,412, 1929, addn. to 545,576; *Chem. Abs.*, 1932, 27, 2541. German P. 584,858, 1933; *Chem. Abs.*, 1934, 28, 1154.

phenol should have at least one of the positions in 2, 4 or 6 of the benzene nucleus substituted and the product should be capable of thermohardening.

Among the examples given by Hönel are the following: melissic palmitate (beeswax) with the liquid product from p-tertiary-amyphenol and formaldehyde; beef tallow with p-tertiary-butyl-m-cresol and formaldehyde; castor oil with p-cresol-formaldehyde; moderately boiled tung oil and linseed oil with thymol-formaldehyde; glycerol succinate-lactate with p-chlorophenol-formaldehyde; glycerol-citrate-ricinoleate-salicylate with p-cresol-formaldehyde; glycerol-phthalate-stearate with the reaction product of o-cresol and methyl ethyl ketone; and guaiacol-formaldehyde with glycerol-abietae-sebacate. Other examples include glycerol-phthalate-linoleate-abietae with butylphenol-formaldehyde; phthalic anhydride, ricinoleic acid and mannite mixture with o- and p-chloro-m-cresol; phthalic anhydride, methylcyclohexanol, glycerol with di-chloro-diphenylolpropane and formaldehyde; and citric acid and benzyl alcohol with oleic acid and glycerol. The properties of these condensation products range from that of an oily liquid to one of rubber-like consistency.

Lacquers containing phenol-formaldehyde and alkyd resins may be coated on a metal surface and, after the film has hardened, a top coat of a nitrocellulose lacquer can be applied. The alkyd resins should contain some fatty acids, especially those derived from linseed oil or castor oil. Moreover, it is advantageous to add to the initial coating an acid catalyst (sulphuric acid in alcohol) to facilitate hardening.<sup>9</sup> Both the transparency and the hardness of the finish obtained are improved by this means. A lacquer prepared from a phenol-free phenol-formaldehyde resol-modified alkyd resin dries and hardens better than one which contains free phenol. The purification of the resol may be accomplished by extracting with water. The lacquer, which consists of 12.5 parts of purified phenol-formaldehyde resol and 50 parts of a linseed oil-modified glycerol phthalate in 48 parts of butyl acetate, 16 parts of ethyl acetate, 16 parts of butanol and 7 parts of ethanol, can be brushed, sprayed or dipped, and stoved at 80-100°C.<sup>10</sup> It is also possible to heat a natural resin (rosin) with a phenol-formaldehyde product and an alkyd resin, either or both of which may be prepared *in situ*. The products have high melting points, dissolve readily in drying oils and act to form varnishes.<sup>11</sup>

Moore and Zucker<sup>12</sup> have described a somewhat similar composite resin for varnish manufacture. It is formed from glycerol phthalate-linoleate and a soluble phenol-aldehyde or phenol-ketone resin. The resins are all readily soluble in low-boiling solvents. Megson and Holmes<sup>13</sup> recommend heating the phenol and paraformaldehyde with glycerol and a polybasic acid (or its anhydride) at 185°C. for 9 hours in the absence of catalysts, to yield resins. The addition of relatively small proportions of phenol-formaldehyde to glycerol phthalate resin was found by Peterson<sup>14</sup> to accelerate the curing of the latter. The resulting material had less tendency to soften under heat. Condensation products of naphthols with aldehydes can be used with alkyd resins.<sup>15</sup>

<sup>9</sup> N. Strafford, E. E. Walker and W. J. Jenkins, British P. 312,304, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 980. French P. 669,390, 1929; *Chem. Abs.*, 1930, 24, 1753.

<sup>10</sup> N. Strafford and E. E. Walker, U. S. P. 1,977,552, Oct. 23, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 254. British P. 308,048, 1928; *Chem. Abs.*, 1930, 24, 253. French P. 669,612, 1928; *Chem. Abs.*, 1930, 24, 1905.

<sup>11</sup> W. J. R. Evans and R. Hill, British P. 367,001, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B.*, 1933, 437. French P. 731,340, 1932; *Chem. Abs.*, 1933, 27, 858. See also A. A. Drummond and H. H. Morgan, British P. 413,718, 1932, to Imperial Chem. Ind.; *Brit. Chem. Abs. B.*, 1934, 897.

<sup>12</sup> C. G. Moore and M. Zucker, U. S. P. 1,867,583, July 19, 1932, to Glidden Co.; *Chem. Abs.*, 1932, 26, 5221. See U. S. P. 1,867,584, July 19, 1932, to Glidden Co.; *Chem. Abs.*, 1932, 26, 5221.

<sup>13</sup> N. J. L. Megson and E. L. Holmes, British P. 268,366, 1931; *Brit. Chem. Abs. B.*, 1932, 475.

<sup>14</sup> C. F. Peterson, British P. 250,949, 1926, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1927, 21, 1265. See French P. 768,031, 1934, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1935, 29, 524.

<sup>15</sup> French P. 742,154, 1933, to Compagnie nationale Nord réunies (Établissements Kuhlmann) and Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 27, 3629. See also French P. 745,603, 1933, to Resines et vernis artificiels (Soc. anon.); *Chem. Abs.*, 1933, 27, 4431.



The phenol-aldehyde-alkyd resins have been formed in the presence of boric acid to yield products which are of a sensibly neutral character, of good consistency and body and which are compatible with nitrocellulose and other cellulose esters. The resins are prepared by heating to 240°C. 148 g. of phthalic anhydride, 31 g. of boric acid and 150 g. of glycerol together with 50 g. of a phenol-formaldehyde condensate containing an organic salt of zinc. The reaction is carried out in the presence of a solvent or flux which consists of natural resins and drying or non-drying oils.<sup>16</sup>

Bielouss<sup>17</sup> has developed phenol-formaldehyde-alkyd resins with the following characteristics: solubility in drying oils with the capacity of forming quick-drying varnish; miscibility with nitrocellulose solutions to give durable lacquers for interior and exterior exposure and compatibility with other cellulose esters. Alkyd resins, when prepared in the presence of certain carboxylic acids of high molecular weight, are said to be insoluble in vegetable oils, which limits their usefulness in oil varnishes; they are, however, compatible with cellulose esters. Phenol-aldehyde resins, on the other hand, when fused with natural gums (rosin) are readily soluble in drying oils, but have a very restricted use with cellulose lacquers, due to limited compatibility, odor, brittleness of the resulting film and discoloration when exposed to the atmosphere. The combination of these two types of resin was found to give the required properties. As an example, 50 parts of phenol, 30 parts of phthalic anhydride and 65 parts of rosin were heated to 110°C., and to the molten mixture were added 17 parts of formaldehyde; heating being continued for 1 hour. The esterification of the free acids is then accomplished by adding 21 parts of glycerol and heating for 2 hours at 250°C. The acidity of the resulting resin is 11. Such a resin is soluble in oils and may be incorporated into cellulose acetate or nitrocellulose solutions with the formation of clear, durable lacquers. The order of carrying out the operation may be varied; the rosin-cresol-formaldehyde product can be esterified with glycerol at 270°C. and the resulting resin heated with the glycerol phthalate.

Bruson<sup>18</sup> has described a series of rubber-like resins, obtained by condensing a polyhydric alcohol (glycerol) with long-chain dibasic aliphatic acids (adipic,  $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ , to sebacic acid,  $\text{HOOC}-(\text{CH}_2)_{10}-\text{COOH}$ ). When a phenol-formaldehyde resin is mixed with a solution of one of these alkyd condensation products in alcohol, acetone, ethyl or butyl acetate, homogeneous solutions result which yield tough, adherent and flexible films that retain their flexibility even when baked for a long time. Such films in either the baked or the unbaked state are insoluble in oils or hydrocarbons and may be used for coating oil-storage tanks, a case in which elasticity of the film is of prime importance.

In manufacturing a resin of this type 100 parts of a soluble Novolak phenol-formaldehyde resin are dissolved in 200 parts of alcohol and mixed with 50 parts by weight of the soluble rubbery condensation product prepared by heating glycerol with sebacic acid. A clear solution results which forms films on evaporation. Resins other than the phenol-formaldehyde may be plasticized in the same manner. These include shellac, cresol-formaldehyde resins, ketone-formaldehyde resins and condensation products of phenol with furfural as well as formaldehyde-urea resins. Instead of preparing a solution of the two resin components, the solid, hard, brittle resin may be powdered and mixed directly with the viscous rubbery condensation products in a mixer to yield a pasty mass which may be molded.

Phenol-formaldehyde condensation products containing carboxylic groups are

<sup>16</sup> I. Rosenblum, U. S. P. 1,969,761, Aug. 14, 1931; *Chem. Abs.*, 1934, 28, 6330. See I. Rosenblum, British P. 416,476, 1934; *Chem. Abs.*, 1935, 29, 1176. French P. 738,444, 1932; *Chem. Abs.*, 1933, 27, 1775.

<sup>17</sup> E. Bielouss, U. S. P. 1,866,962, July 12, 1932, to Henry A. Gardner Laboratory, Inc.; *Chem. Abs.*, 1932, 26, 4726.

<sup>18</sup> H. A. Bruson, U. S. P. 1,732,166, Nov. 25, 1930, to Resinous Products & Chemical Co.; *Brit. Chem. Abs. B*, 1931, 687.

formed in the reaction of a phenol-formaldehyde resin with a halogenated aliphatic acid (chloroacetic acid) or by the reaction of a phenoxy aliphatic acid (cresoxy-acetic acid) with formaldehyde. The product is a "resin acid," and when it or its ammonium or amine salt is heated with a polyhydric alcohol above 100°C. a hardened mass is formed. Mixed with fillers, this may be used for making laminated products.<sup>19</sup> An example is given in which an alkaline solution of a condensation product from a mixture of cresols and formaldehyde is treated with sodium chloroacetate. The resinous product is precipitated by acidifying, and is then condensed with glycerol. A resin is obtained which becomes insoluble and infusible, but which remains elastic, when heated to 150-170°C. Polyvinyl alcohol and water-soluble carbohydrates may take the place of glycerol.<sup>20</sup>

The condensation products of polybasic aliphatic acids with hydroxyalkyl ethers of polyhydric alcohols may be mixed with unhardened or incompletely hardened phenol-aldehyde condensation products and the mixture subjected to a hardening process. The products obtained are less brittle than those from the corresponding phenol-aldehyde resins alone, and may be used for making films, plastic masses and lacquers. Suitable condensation products are obtainable from succinic acid and glycerol trihydroxyethyl ether or sorbitol polyhydroxyethyl ether. Aromatic or hydroaromatic acids may be used in place of the aliphatic acid.<sup>21</sup>

A resin for cementing glass, metals and wood is prepared by heating benzoic or cinnamic acid with glycerol and cyclohexanol in the presence of phenols and aldehydes. The material obtained is dehydrated by heating under reduced pressure.<sup>22</sup> Glass sheets and sheets of cellulose or cellulose acetate compositions may be united by means of resins formed from phthalic anhydride (with succinic) and glycerol and from phenols and formaldehyde at the "A" stage of condensation, with or without further treatment with resin acids such as abietic acid. Nitrocellulose, dissolved in a solution of the mixed resins, assists cohesion.<sup>23</sup>

Xylenol-aldehyde resins have been incorporated into glycerol phthalate and into the rosin-glycerol phthalate condensation products. A mixture consisting of 61 parts of the technical xylenols, 83 parts of formalin and 2.5 parts of sodium hydroxide solution were heated to boiling for 30 minutes, cooled, the aqueous layer decanted and then reheated to 70°C. in order to clarify the solution. The xylenitic resin was then incorporated with 148 parts of rosin, 63.1 parts of phthalic anhydride and 48.4 parts of glycerol and heated to 280-290°C. for 45 minutes, followed by steaming for 1 hour at 250-260°C. The softening point of this resin was 155-160°C. and it was compatible with nitrocellulose. A solution of 20 parts of the xylenol-aldehyde modified alkyd resin and 5 parts of half-second nitrocellulose in 10 parts of butyl alcohol, 20 parts of butyl acetate and 30 parts of toluene yielded hard, brilliant films which were relatively light-stable.<sup>24</sup>

#### MODIFICATION BY PHENOL-FURFURAL RESINS

The combination of polybasic acid-polyhydric alcohol resins with furfural-phenol resins was developed by Weber.<sup>25</sup> A molding mixture is prepared by dissolving

<sup>19</sup> British P. 298,085, 1928, and 326,214, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 520.

<sup>20</sup> A. Voss, German P. 473,171, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 3115. French P. 701,722, 1930; *Chem. Abs.*, 1931, 2, 4096.

<sup>21</sup> O. Schmidt and E. Meyer, German P. 538,323, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1812. French P. 708,811, 1931; *Chem. Abs.*, 1932, 26, 1077. German P. 545,636, 1930, addn. to 538,323; *Chem. Abs.*, 1932, 26, 3687.

<sup>22</sup> L. C. Pechin, French P. 722,128, 1931; *Chem. Abs.*, 1932, 26, 4191.

<sup>23</sup> J. E. Alcock, British P. 319,873, 1928; *Chem. Abs.*, 1930, 24, 2568.

<sup>24</sup> Carleton Ellis, U. S. P. 1,907,832, July 24, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 6003.

<sup>25</sup> H. C. P. Weber, U. S. P. 1,715,888, June 4, 1928, to Westinghouse Electric & Mfg. Co.; *Chem. Abs.*, 1929, 23, 3823. British P. 233,519, 1925, to Metropolitan-Vickers Electrical Co., Ltd.; *Chem. Abs.*, 1927, 21, 2687.

10-30 parts of the phenol-furfural resin in about 10 parts of alcohol and adding a solution of 70-90 parts of the glycerol resin component dissolved in 10 parts of alcohol. Twenty parts of a filler (e.g., mica or wood flour) are incorporated and the solvent is removed by evaporation. The dried, impregnated composition is then finely ground, and may be converted into an insoluble infusible stage by molding with heat and pressure. Instead of mixing solutions of the resins, the solids may be mixed, either with or without a filler, and hot-molded as before. In cases where a varnish is required, an alcoholic solution is employed. Both the molded products and films or impregnated materials have excellent insulating properties.

The properties of the blended resin probably result from a mutual condensing action of the resins upon each other, inasmuch as the resin can be brought to the infusible stage, that is, the "C" stage much more easily than if the composition were merely a mixture of the two resins. The final product retains the good insulating and resistant properties of the alkyd resin, together with the ease of molding of phenol-furfural resins.

#### MODIFICATION BY UREA-FORMALDEHYDE RESINS

As has already been mentioned,<sup>26</sup> colorless resins are formed by condensing urea with formaldehyde. These resins harden rapidly under the influence of heat but they lack flexibility when so hardened and are only sparingly soluble in such common solvents as acetone and toluene. Hill and Walker<sup>27</sup> have employed urea-formaldehyde resins as modifying agents for the alkyd resins, and have developed in this way products which are said to harden very readily under various conditions. First, an alkyd resin is prepared by heating together 148 parts of phthalic anhydride, 62 parts of glycerol and 150 parts of castor oil at 190-200° for 45 minutes. The product is a pale yellow, tough, flexible and moderately hard resin which is soluble in ketones, esters, hydrocarbons and in hot alcoholic solvents. After dissolving 14 parts of this resin in 14 parts of butyl alcohol, and adjusting the hydrogen-ion concentration to  $10^{-6}$  by adding alcoholic caustic potash, 3 parts of urea are added. The solution is heated to dissolve the urea and then 3 parts of paraformaldehyde are added and the mixture refluxed for a short time. The resulting solution is diluted with 10 parts of solvent naphtha and traces of suspended matter are filtered off. The product is a clear, pale yellow liquid from which the resin may be isolated by vacuum evaporation at low temperatures. On baking, transparent colorless coatings are obtained which possess good adhesion, flexibility, hardness and toughness. This resin is compatible with nitrocellulose, and may be employed as a component in lacquers.

Dimethylolurea itself may be employed and thiourea may be used in place of urea. The components are said to react chemically and do not form a simple mixture. As little as 5 per cent of the urea-formaldehyde condensation product exerts a considerable modifying action on the alkyd resin. The choice of the components of the polyhydric alcohol-polybasic acid resin is controlled by the purpose for which the product is intended. When hardness in the final material is the chief consideration, an unmodified glycerol phthalate condensation product should be employed. When flexibility and light color are desired a castor oil-modified alkyd resin serves the purpose. Incorporation of a drying oil fatty acid is likely to result in a degradation of color. Small amounts of inorganic

<sup>26</sup> See Chapter 26, *et seq.*

<sup>27</sup> R. Hill and E. E. Walker, U. S. P. 1,877,130, Sept. 13, 1932, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 27, 300. British P. 344,401, 1939; *Brit. Chem. Abs. B*, 1931, 597. German P. 594,197, 1934; *Chem. Abs.*, 1934, 28, 3603. French P. 694,181, 1930; *Chem. Abs.*, 1931, 25, 2013.

acid may be used in preparing the final product; this allows drying at room temperature.

Thus, to 100 parts of the alkyd resin (castor oil-modified, just described) dissolved in 200 parts of glycol monoethyl ether, 100 parts of dimethylolurea are added and the mixture refluxed for 30 minutes; 85 parts of methylated spirits (ethanol denatured with methanol) and 85 parts of toluene are then added. Sixty parts of the resulting lacquer are treated with 0.42 part of a 10 per cent solution of sulphuric acid dissolved in a mixture consisting of 2 parts of glycol monoethyl ether, 1 part of toluene and 1 part of methylated spirit. A lacquer of this type, containing a small amount of acid, dries rapidly at ordinary temperatures, whereas one without acid requires heat treatment for rapid hardening to take place. Besides sulphuric acid, sodium hydrogen sulphate, chlorosulphonic acid, sulphuryl chloride, hydrochloric acid, trichloroacetic acid, tartaric acid, boric acid and malic acid are effective.

Goldschmidt and Mayrhofer<sup>28</sup> have produced modified alkyd resins by adding the liquid or viscous condensation products from phthalic anhydride and polyhydric alcohols to an aqueous suspension of urea and formaldehyde. The addition is made prior to, during or after formation of a condensation product by heating in presence of 2 *N* sulphuric acid. The products can be hardened in molds at a temperature higher than normal without danger of cracking and are transparent and vitreous. The ratio of the weights of urea and phthalic anhydride must be considerably greater than unity and an acid or an alkaline condensing agent may be present. It is also possible to include a phenol in the reaction mixture in carrying out the above condensation.<sup>29</sup> Colored lacquers, made from synthetic resin compositions of glycerol phthalate-formaldehyde-urea (or -thiourea) and dyes (Cardinal Red J) may be used for producing colored electric-light bulbs. The lacquer is applied to the bulbs by dipping and the coating hardened by the normal heat of the lamp.<sup>30</sup>

Condensation of urea and formaldehyde in aqueous solution may be carried out to yield an initial product, to which is added, after concentration, a polyhydric alcohol-polybasic acid resin. The solution is further concentrated, dried *in vacuo*, and may then be molded under heat and pressure. Thiourea may be substituted for part of the urea. In the initial condensation the  $p_H$  is adjusted to between 5 and 6 by adding triethanolamine. A sufficient quantity of the alkyd resin is then added to lower the  $p_H$  to between 3.5 and 5.0.<sup>31</sup> A similar product<sup>32</sup> is obtained by adding less than 1 mol of urea to 2.25 mols of formaldehyde, the  $p_H$  of which has been adjusted to between 6 and 7 by addition of an organic base (triethanolamine). The mixture is heated under reflux until spontaneous boiling ceases, whereupon more urea is added and the product concentrated to a thick syrup by evaporation in the open. The  $p_H$  is then adjusted to 7-7.5, and thiourea added in the ratio of 1 mol to 2 mols of the remaining uncombined formaldehyde. The product is again boiled and concentrated. An alkyd resin (or other plasticizer) is added and the  $p_H$  adjusted to between 3 and 5. The product is then dried *in vacuo* and ground. Resinous condensation products from urea or its derivatives and paraformaldehyde may also be formed in presence of organic compounds such as colophony, copal, amines, in addition to the alkyd resins. Anthracene and chlorinated or nitrated naphthalenes serve as plasticizers for these products.<sup>33</sup>

<sup>28</sup> S. Goldschmidt and R. Mayrhofer, *British P.* 316,144, 1929; *Chem. Abs.*, 1930, 24, 1711. *German P.* 572,367, 1928; *Chem. Abs.*, 1933, 27, 3044.

<sup>29</sup> *German P.* 536,169, 1927, to Jaroslaw's Erste Glimmerwaren-Fabrik; *Chem. Abs.*, 1931, 25, 4422. *British P.* 272,947, 1928; *Chem. Abs.*, 1928, 22, 1833. *French P.* 635,745, 1927; *Chem. Abs.*, 1928, 22, 4740. See *German P.* 493,184, 1926; *Chem. Abs.*, 1930, 24, 2846.

<sup>30</sup> E. A. Bevan, *British P.* 349,100, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1931, 726. *French P.* 712,751, 1931; *Chem. Abs.*, 1932, 26, 1741.

<sup>31</sup> *British P.* 337,357, 1929, to Toledo Scale Mfg. Co.; *Chem. Abs.*, 1931, 25, 2318.

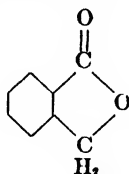
<sup>32</sup> *British P.* 345,935, 1929, to Toledo Scale Mfg. Co.; *Brit. Chem. Abs. B*, 1931, 642.

<sup>33</sup> *British P.* 318,859, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1930, 24, 2624.

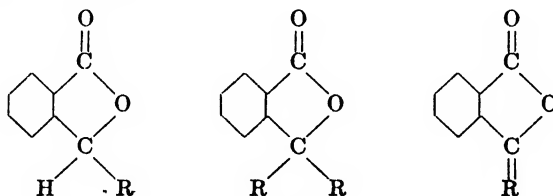
Howald<sup>44</sup> has prepared a resin by reacting 1 mol of ammonium thiocyanate with 1.5-2 mols of formaldehyde, the excess formaldehyde being condensed with urea, thiourea or resorcinol during the molding operation. The resin was plasticized by a polybasic acid-polyhydric alcohol ester so prepared as to contain free carboxyl groups.

#### PHTHALIDES AS MODIFYING AGENTS

The use of phthalides as modifying agents for alkyds and other synthetic resins has been developed by Jaeger.<sup>45</sup> Phthalide<sup>46</sup> (m.p. 83°C., b.p. 290°C.), the lactone or internal ester of o-carboxybenzyl alcohol of the structure



possesses desirable softening properties when incorporated into alkyds. It is also non-corrosive, relatively non-volatile and satisfactorily withstands the temperatures required in molding. Hexahydrophthalide (b.p. 134-138°C. at 25 mm.) is a much more fluid compound than phthalide itself and is a colorless, odorless, heavy oil. Other derivatives include the mono- and disubstituted phthalides, as well as the alkylidene phthalides.



The method of using the phthalide is as follows: to 85 parts of glycerol phthalate resin, which is freshly prepared and fairly hard but not infusible, are added 15 parts of phthalide and the mixture heated to 150°C. until a homogeneous mass is obtained.

Among the polyhydric alcohols used in preparing the alkyd resin to be modified by phthalides, glycerol and glycol are of the greatest commercial importance, although others may be employed, among which are butylene glycol, mannitol and glycol propyl ether. Phthalic anhydride is the most important dicarboxylic acid, though substituted phthalic acids, sebacic or succinic acid, give similar results. Other acids, such, for example, as the monocarboxylic acids, may also be incorporated in the alkyd resin.

The following example illustrates the method of preparing a resin of this type: 1 mol of glycerol and 1 mol of phthalic anhydride are heated at 180°C. until gas evolution ceases; 1 mol of phthalide is then added and the mixture is heated at 210°C. until a test portion on a glass rod solidifies to a hard product which is not

<sup>44</sup> A. M. Howald, U. S. P. 1,910,338, May 23, 1933, to Toledo Synthetic Products, Inc.; *Brit. Chem. Abs.* B, 1934, 109. See British P. 873,184, 1931, to Toledo Synthetic Products, Inc.; *Brit. Chem. Abs.* B, 1932, 737.

<sup>45</sup> A. O. Jaeger, U. S. P. 1,860,098, May 24, 1932, to the Selden Co.; *Chem. Abs.*, 1932, 26, 3945. Canadian P. 321,652, 1932; *Chem. Abs.*, 1932, 26, 5393. German P. 539,740, 1929; *Chem. Abs.*, 1932, 26, 2233. French P. 874,012, 1929; *Chem. Abs.*, 1930, 24, 2622.

<sup>46</sup> A. O. Jaeger, U. S. P. 1,941,474, Jan. 2, 1934, to the Selden Co.; *Chem. Abs.*, 1934, 28, 1890.

sticky. The resin is then mixed with an equal weight of phenol-formaldehyde or phenol-furfural resin, capable of being hardened by heat, together with a wood-flour filler and a pigment. This admixture is best made by grinding in the dry state. After adding 5 per cent of dibutyl phthalate, the product is hot-molded. Products are obtained which have excellent strength and which will take a high polish.

A resin obtained from 2 mols of glycerol, 2 mols of phthalic anhydride, 1 mol of phthalide and 1 mol of benzoic acid may be incorporated with half its weight of a formaldehyde-urea or formaldehyde-urea-thiourea resin. Again, a resin containing 1.5 mols of phthalic anhydride, 1.5 mols of phthalide or ethylphthalide and 1.0 mol of the fatty acids of coconut oil, is soft and flexible. Mixed with an equal proportion of a vinyl resin and dissolved in a solvent, a solution for impregnating paper results. Other synthetic resins may also be incorporated, among which are amine drying oils of the tung oil-toluidine type, aminoketone resins, polymerized styrene or itaconic acid resins. In general the phthalide-modified resins are soluble in the solvents which will dissolve the unmodified resin as well as in additional solvents. This range of solubility adds greatly to the adaptability of these resins for coating compositions. The phthalide-modified alkyd resin in its fusible stage is soluble in alkyd resin solvents and may be blended with nitrocellulose.<sup>37</sup> An impregnating varnish is thus obtained which leaves film of excellent quality without the use of any plasticizer. Where maximum flexibility is needed, an amount of dibutyl phthalate or ethyl benzoylbenzoate equal to about 5-10 per cent of the weight of resin may be added. A soft, balsam-like resin is obtained with 1.5 mols of ethylene glycol, 1 mol of phthalic anhydride and 1 mol of phthalide or hexahydrophthalide.<sup>38</sup>

#### MISCELLANEOUS RESINS

Hovey<sup>39</sup> has tabulated the means by which alkyd resins may be made compatible with or blended with other plastic materials. Due to the many types of alkyds and to the variation in naturally occurring materials with which these resins may be used, certain minor discrepancies will occur; the table nevertheless serves as a useful guide. See page 943.

Natural or artificial rubber may be mixed with resinous esters of mono- or polybasic acids with polyhydric alcohols before vulcanization in order to increase the strength of the product. Thus, for example, acids such as abietic, phthalic or palmitic may be esterified with glycols or with ethylene oxide and the products added to the rubber in the proportion of about 2 per cent.<sup>40</sup> Coating and adhesive compositions may be manufactured from the oily polymerization products of diolefins (butadiene) polymerized without the aid of alkali metals. The oil is incorporated with synthetic resins, among which are those of the alkyd type. Cellulose ethers and esters, drying oils, natural resin, fillers and vulcanizing agents may also be added.<sup>41</sup> Addition of drying oil-modified alkyds to the lacquers prepared from chlorinated rubber improves the films.<sup>42</sup>

An adhesive for uniting celluloid to glass prepared by Ford and McCarroll<sup>43</sup> consists of polyvinyl acetate, glycerol phthalate and a plasticizer. Products used

<sup>37</sup> A. O. Jaeger, U. S. P. 1,804,909, June 28, 1932, to the Selden Co.; *Chem. Abs.*, 1932, 26, 4488.

<sup>38</sup> For resins plasticized with hexahydrophthalide, see A. O. Jaeger, U. S. P. 1,892,784, Jan. 3, 1933, to the Selden Co.; *Chem. Abs.*, 1933, 27, 2298.

<sup>39</sup> A. G. Hovey, *Ind. Eng. Chem.*, 1933, 25, 613.

<sup>40</sup> British P. 323,322, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 3134.

<sup>41</sup> British P. 339,944, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 118.

<sup>42</sup> L. Rosenthal and G. Schultze, *Färb.-Chem.*, 1934, 5, 53; *Brit. Chem. Abs. B*, 1934, 636.

<sup>43</sup> H. Ford and R. H. McCarroll, British P. 365,828, 1930; *Chem. Abs.*, 1933, 27, 2260. M. Sakama (Japanese P. 101,092, 1933; *Chem. Abs.*, 1934, 28, 4849) has also prepared an adhesive from glycerol phthalate and polyvinyl acetate. For alkyd resins modified with polyvinyl halides see F. Oschats, German P. 607,555, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 4194.

TABLE 46.—Miscibility of Alkyd Resins.

Materials	Methods of Blending with Alkyd Resins <sup>*</sup>
Mastic . . . . .	a, b, c, d
Dammar . . . . .	a, b, c, d
Rosin . . . . .	a, b, c, d
Shellac . . . . .	c, d
Copal . . . . .	a, c
Rubber (smoked sheet) . . . . .	a, c, e
Water glass . . . . .	f
Glue . . . . .	c, f
Thus . . . . .	a, b, c, d
Pitches . . . . .	c, e
Casein . . . . .	c, f
Chicle . . . . .	c, d
Rubber latex . . . . .	c, f
Nitrocellulose . . . . .	c, d
Pine tar . . . . .	a, b, c, d
Canada balsam . . . . .	a, b, c, d
Drying oils . . . . .	a, b, c, d, f
Phenolic type of resin . . . . .	a, c, d
Urea resins . . . . .	a, c, f
Vinyl acetate . . . . .	c, d
Paracumarone resins . . . . .	a, b, c, d

<sup>\*</sup> a. Cooking with other ingredients in preparation of alkyd resin complex.

b. Simple heat-blending

c. Hot mixing on rollers, in dough mixers, or in Banbury mixers.

d. Dissolving both in a common solvent or miscible solvent

e. Dissolving both in a common solvent or miscible solvent provided that the resin is of hydrocarbon-soluble type

f. Using an aqueous ammonia or triethanolamine solution

for molding are obtained by mixing polymerized vinyl chloride and alkyd resins, preferably of the flexible type. Among the fillers which may be used are the oxides of zinc or titanium.<sup>44</sup> Polymerized acrylic acid derivatives, such as the allyl or methyl esters, are improved by the incorporation of esters of polybasic acids and polyhydric alcohols (monoacetin  $\beta$ -methoxyethyl phthalate). They are then more suitable for use in safety glass.<sup>45</sup>

Solutions of polymerized styrene and natural or synthetic resins compatible with it are used in the manufacture of varnishes. Among the resins which may be used are those of the linseed oil-alkyd type.<sup>46</sup>

Moore and Zucker<sup>47</sup> used a mixture of 35 parts of phthalic anhydride, 22.5 parts of linseed oil acids and 17.5 parts of glycerol and in addition 25 parts of cumarone resin. The latter allows the reaction to proceed without danger of gelation, thus allowing more complete interaction; it also imparts some water-resistance and lowers the acid number. Larger amounts of cumarone resin impart brittleness unless the oil content is increased.

Gardner<sup>48</sup> has found that incorporation of chlorinated biphenyl<sup>49</sup> with alkyd resins or other types of synthetic resin accelerates their speed of drying. A resin is first made by heating 100 parts of phthalic anhydride and 32 parts of glycerol to temperatures below 190°C., and to the resulting fluid mass are added with stirring 25 parts of chlorinated biphenyl (containing 50-60 per cent of chlorine).

<sup>44</sup> French P. 740,186, 1932, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 27, 2320. German P. 601,323, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 7564.

<sup>45</sup> British P. 355,712, 1930, to Röhm & Haas A.-G.; *Brit. Chem. Abs. B.*, 1932, 72.

<sup>46</sup> British P. 375,320, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 807.

<sup>47</sup> C. G. Moore and M. Zucker, U. S. P. 1,915,544, June 27, 1933, to Glidden Co.; *Chem. Abs.*, 1933, 27, 4451. Canadian P. 348,042, 1933; *Chem. Abs.*, 1935, 29, 8423.

<sup>48</sup> H. A. Gardner, U. S. P. 1,867,078, Nov. 13, 1932; *Chem. Abs.*, 1933, 27, 1530. British P. 351,637, 1930; *Chem. Abs.*, 1932, 26, 8125.

<sup>49</sup> See Chapter 56.

The product is a light-colored resin which may be admixed with the usual varnish oils. These films dry so rapidly that successive coatings may be applied at intervals of 30 minutes. The resulting composite is then baked and is said to serve as an undercoat for nitrocellulose lacquers. A mixture of alkyd resins and chlorinated biphenyl has also been suggested for use in safety glass.<sup>60</sup>

Compositions with improved water-resistance are reported obtainable by modifying alkyd resins with ketenes.<sup>61</sup> The resin is dissolved in ethyl alcohol or acetone and the ketene added either as a gas or in solution if it is of high boiling point.

Casein plastics are usually prepared by first extruding a casein mass with approximately 20 per cent of water through a heated screw press and then hardening the extruded mass with formaldehyde. By combining casein with alkyd resins and treating with formaldehyde, a mass results which when dried and powdered can be hot-molded. The procedure is as follows: 25 parts of a castor oil-modified glycerol phthalate are added to 75 parts of water containing 2.67 parts of a 28 per cent solution of ammonium hydroxide. Seventy-five parts of casein are dissolved in 1000 parts of water and warmed at 60°C. and concentrated ammonium hydroxide added until a smooth dispersion is obtained. The solutions of casein and resin are mixed and precipitated with dilute, 25 per cent hydrochloric acid. After the precipitate has settled 200 parts of 37 per cent formaldehyde are added and the mass allowed to stand for 48 hours. It is then washed, dried, comminuted and molded.<sup>62</sup>

Protein-modified resins may be made by heating gelatin or casein with a mixture of glycerol and phthalic anhydride. For example, 35.1 parts phthalic anhydride, 14.9 parts glycerol and 10 parts gelatin are heated for about 5 hours at 200°C. until the product possesses an acid number of 65-70. The resin may be used in safety glass.<sup>63</sup> Another type of modified resin is obtained by use of simple amino acids, the hydrolytic products of proteins.<sup>64</sup>

<sup>60</sup> H. A. Gardner, U. S. P. 1,836,914, Dec. 15, 1931; *Chem. Abs.*, 1932, 26, 1087.

<sup>61</sup> M. M. Brubaker and G. D. Graves, U. S. P. 1,993,828, March 12, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 3071. British P. 419,373, 1934; *Chem. Abs.*, 1935, 29, 2627.

<sup>62</sup> H. S. Holt, U. S. P. 1,978,533, Oct. 30, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 252. See British P. 419,293, 1933; *Brit. Chem. Abs. B*, 1935, 70.

<sup>63</sup> C. Sly, U. S. P. 2,009,029, July 23, 1935, to E. I. du Pont de Nemours & Co. For the use of dry yeast in alkyd resin molding compositions see W. Mooser-Schiess, U. S. P. 1,317,721, Oct. 7, 1919; *Chem. Abs.*, 1919, 13, 3289.

<sup>64</sup> M. M. Brubaker and R. E. Thomas, U. S. P. 2,009,432, July 30, 1935, to E. I. du Pont de Nemours & Co.



## Chapter 46

### Alkyd Resin Salts

Under strenuous alkaline conditions the polyhydric alcohol-polybasic acid resins are completely saponified. Mild alkaline treatment, however, gives rise to products which can be used in the form of aqueous solutions or dispersions as coating, impregnating or cementing compositions and as plastic materials. The important factors in the preparation of the water-soluble alkyd resins are first the acid number of the resin and second the amount of alkali used in the neutralization. Resins of low acid number are dispersed or emulsified in the presence of alkalies. With resins of a high acid number, a small amount of alkali causes dispersion or emulsification, but a large amount of alkali, that is, equivalent to the acid number of the resin, results in the formation of a clear water solution in which the salts of the resin are soluble. The neutralization may be achieved by treating a water-insoluble resin of the glycerol phthalate type, prior to the formation of the final hard insoluble modification, with an aqueous solution of either inorganic bases (ammonium, potassium, sodium, calcium or barium hydroxide or sodium sulphide) or with organic bases (hexamethylenetetramine, toluidine or aniline).<sup>1</sup> For example, 60 parts by weight of castor oil-phthalic glyceride resin are heated to 110°C. and poured slowly, with agitation, into 200 parts of boiling water containing 6 parts of concentrated ammonium hydroxide solution. The resulting resin dispersion can be used for treating paper by brushing, flowing, spraying or dipping.

A resin of acid number 36.5 and melting at 62°C. is prepared from animal tallow fatty acids, 9 parts, phthalic anhydride, 16 parts, and glycerol, 10 parts, by heating at 245-250°C. for 1 hour. By agitating this material in water rendered slightly alkaline with potassium hydroxide, a milky emulsion forms, which when introduced into paper and dried, imparts a glossy surface to the latter.

Cottonseed-phthalic glyceride resin gives favorable results when dispersed in water containing ammonium hydroxide. A dispersion of this type was employed by the author in making a "greaseproof" paper. These compositions are also useful as cementing compositions especially in building up sheets of paper into thick board.

Resins derived from polybasic acids other than phthalic may be used, although the cottonseed-phthalic glyceride resin is outstanding in this respect because of its cheapness, the ease with which emulsification takes place and its excellent grease- and water-repellent properties. The stearic resins are harder, whereas oleic resins are inclined to be soft and somewhat sticky. Benzoic-phthalic glyceride is more difficult to emulsify with aqueous ammonium hydroxide; an aqueous medium containing 3 per cent each of ammonium hydroxide and gum arabic yields a better emulsion in this instance. Other emulsifying agents include gum tragacanth and Irish moss.

<sup>1</sup> British P. 368,997, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 1774. French P. 698,598, 1930; *Chem. Abs.*, 1931, 25, 3186.

Bradley<sup>2</sup> has described a related method of treating a glycerol-phthalic anhydride resin with ammonia in order to render it water-soluble. The resin itself was prepared by heating a mixture of 90 per cent glycerol, 63 parts, and phthalic anhydride, 148 parts, at 150-230°C. until, on cooling, a sample set to a resin softening at 85-100°C. and had an acid number of from 100-150. Fifty parts of this resin are then agitated with 100 parts of water and 6.5 parts of 46 per cent ammonium hydroxide until the resin has dissolved in the water to form a clear solution. This reaction may be carried out at room temperature, but takes place more quickly at an elevated temperature. Other alkalies (sodium or potassium hydroxides) and also organic bases (ethanolamines) gave similar results. By allowing the aqueous solution of the resin to flow on to tissue paper and drying at 80°C. for 10 minutes, the paper became transparent. A greatly enhanced water-resistance was imparted to the paper by treatment with a dilute solution of acetic acid before drying; the resin is rendered water-insoluble by the acid.

Other resins, derived either from polyhydric alcohols and polycarboxylic acids alone or admixed with monobasic acids, were found by Bradley to give similar results; among these may be mentioned the resins from glycerol, phthalic anhydride and linseed oil fatty acids, and from ethylene glycol and succinic acid. The aqueous solutions of resins may be used in conjunction with casein. A solution of 32 parts of casein, 160 parts of water and 8 parts of concentrated ammonia is mixed with an equal quantity of one of the resin solutions, applied to the paper and dried at 100°C. for five minutes. A homogeneous, transparent and glossy film is obtained. Its water-resistance is improved by dipping the coated paper in 40 per cent aqueous formaldehyde and drying. It has also been found that these resins may be precipitated from aqueous solutions by water-soluble polyvalent metallic compounds (barium and calcium hydroxides) and salts (alum or iron salts). These insoluble products are metallic glycerol phthalates.

Coating compositions, which form a relatively stable combination with a flattening agent such as aluminum stearate, are prepared by emulsifying with water a solution of glycerol phthalate in an organic solvent. Bentonite, soap or gelatin serve as emulsifying agents.<sup>3</sup> Ethylamine, diethylamine, triethylamine or piperidine react with alkyd resins in water to give a homogeneous solution which is capable of forming a resinous coating on a substratum.<sup>4</sup> The type of alkyd resin may be varied widely. When flexible coatings or films are required, the resin may contain castor oil, olive oil or the fatty acid radicals of such oils. Products yielding coatings which are to harden by exposure to the atmosphere contain linseed oil or linseed oil fatty acid radicals. Table 46A shows the quantities used in preparing some of these resins, together with the acid value of the product and the time in hours for which the ingredients are heated.

The molten resin is poured into the aqueous solution of the base, and stirred until a homogeneous solution results. The resin ingredient, 40 parts, may also be heated with 6.5 parts of piperidine at 60°C. for 30-40 minutes, and the product so obtained dissolved in water. The water solutions when applied to a surface give clear, hard, adherent films on stoving for 1 hour at 100°C. If the resins are treated with an alkali hydroxide or salt of a weak acid (sodium carbonate

<sup>2</sup> T. F. Bradley, U. S. P. 1,780,375, Nov. 4, 1930, to American Cyanamid Co.; *Chem. Abs.*, 1931, 25, 223.

<sup>3</sup> W. Baird, British P. 349,938, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 2071. French P. 708,393, 1930; *Chem. Abs.*, 1932, 26, 1460. A borax solution of the synthetic resin can be mixed in the cold with fillers, pigments and metal salts and oxides to produce a plastic mass which hardens in air and can be used for interior decoration, according to R. C. Korf, German P. 583,176, 1933; *Chem. Abs.*, 1934, 28, 370.

<sup>4</sup> W. Baird, British P. 356,738, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 5778. French P. 713,893, 1931; *Chem. Abs.*, 1932, 26, 3392.

TABLE 46A.—Oil-Modified Alkyds for Aqueous Coatings.

Parts of Glycerol	Parts of Phthalic Anhydride	Parts of Fatty Acid or Fatty Oil	Acid Value	Hours Heating at 180-200°C.
17.6	42.4	40 Castor oil	40	6
11 8	28 2	60 " "	35	3
22.8	47 2	30 Linseed oil	51	4
16 2	23 8	60 " "	70	2
22 8	47 2	30 Oleic acid	47	4.5
16 2	23 8	60 " "	63	1 5
20 6	39.4	40 Tung oil acids	101	4 5
12 0	8 0	80 " " "	87	3
22.8	47 2	30 Stearic acid	44	6
16 2	23 8	60 " "	46	3
(29.5)*	70 5	None	50	5

\* Glycol.

or sodium sulphide) and dissolved in water, the films obtained by drying at 100°C. are water-soluble and may be rendered insoluble by treatment with acids.<sup>5</sup>

Coating compositions intended for baking are obtained by dissolving an alkyd resin (containing an excess of polybasic acid) in dilute ammonium hydroxide and adding enough glycerol so that the solution, when applied to an article and baked, will yield an insoluble resinous coating.<sup>5a</sup>

#### APPLICATIONS OF ALKYD RESIN EMULSIONS AND SOLUTIONS

The alkaline solutions of alkyd resins already described have been applied for stiffening and proofing felt-hat shapes.<sup>6</sup> A solution of this nature is prepared by dissolving 25 parts of the resin formed from heating 31 parts of glycol, 74 parts of phthalic anhydride and 35 parts of castor oil at 185°C. (until the product has an acid value of 95) in 100 parts of 0.39 per cent aqueous ammonia at 60-80°C., and diluting to 250 parts. The impregnated felt is dried to volatilize the ammonia. If metal hydroxides or carbonates are used for dissolving the resin, the felt should be treated with dilute acid either before or after impregnation. Textile materials, other than felt, may be impregnated with a 3 to 35 per cent aqueous solution of an alkyd resin treated with ammonia or a similar base,<sup>7</sup> and then dried or treated with a metallic salt. The latter procedure forms an insoluble derivative of the resin. The elasticity and other physical properties of the textile material are improved in this way.<sup>8</sup>

Alkyd resins have been used to render rubber adaptable to the formation of plastic compositions which are resistant to hydrocarbons. A latex is thoroughly mixed with a solution of alkyd resin in 5 per cent aqueous ammonia. Acetic acid is added and the precipitate is washed with water, dried and finally vulcanized. Rubber dispersions and alkyd resins which have been modified with drying oils or organic acids may also be utilized.<sup>9</sup> A further process for impregnating surfaces makes use of a composition consisting of an aqueous emulsion

<sup>5</sup> W. Baird, British P. 358,095, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 6185. French P. 721,335, 1931; *Chem. Abs.*, 1932, 26, 4191.

<sup>5a</sup> R. T. Ubben, U. S. P. 1,998,744, April 26, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 3864. British P. 422,130, 1935; *Chem. Abs.*, 1935, 29, 3747.

<sup>6</sup> W. Armitage and W. Baird, British P. 358,104, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1931, 1135. French P. 719,469, 1931; *Chem. Abs.*, 1932, 26, 3938. German P. 555,400, 1931; *Chem. Abs.*, 1932, 26, 5217.

<sup>7</sup> Cf. W. Baird, British P. 356,738, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 5778. French P. 718,898, 1931; *Chem. Abs.*, 1932, 26, 3392.

<sup>8</sup> W. Baird and F. J. Siddle, British P. 357,125 and 359,897, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 4726; 1933, 27, 429. French P. 730,534, 1931; *Chem. Abs.*, 1932, 26, 3937.

<sup>9</sup> H. L. Grupe and R. H. Kienle, British P. 395,217, 1932, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1933, 757. French P. 42,447, 1933, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1934, 28, 1221. See Chapter 49.

of a resin of the alkyd type, and rubber, rubber latex or a rubber-like artificial product. The coating consists of alkyd-urea-formaldehyde resin, 11 parts, 30 parts of alkyd resin, 14 parts of solvent naphtha, 45 parts of butyl alcohol, 10 parts of rubber-substitute emulsion and 65 parts of water. The alkyd resin is prepared from 148 parts of phthalic anhydride, 62 parts of glycerol and 150 parts of castor oil at 190-200°C. To 10 parts of the castor oil-modified alkyd resin dissolved in 20 parts of glycol monoethyl ether are added 10 parts of dimethylolurea and the mixture heated. The two modified-alkyd resins are dissolved in the organic solvents, water is added to the rubber-substitute emulsion and the two solutions are mixed and passed through a colloid mill.<sup>10</sup> The emulsion thus obtained is applied by coating, dipping, spreading or spraying and is dried above 90°C. to form a pale-colored coating which has excellent flexibility, weathering properties and a semi-glossy appearance. Chloroprene can also be treated with a water-soluble salt of a glycerol phthalate resin to form an emulsion.<sup>11</sup>

#### VARIOUS APPLICATIONS

Emulsified alkyd resins can be used in the production of paints.<sup>12</sup> When glycerol, 368 parts, linoleic acid, 834 parts, and phthalic anhydride, 518 parts, are condensed together, a soft resin is formed, 100 parts of which are emulsified with 1-2 parts of the ammonium salt of diisopropyl-naphthalene-sulphonic acid. One hundred parts of bleached montan wax are then treated with 4 parts of ammonia in 100 parts of water and mixed with the aqueous emulsion of the resinous body. Finally 150 parts of red iron oxide are incorporated into the mixture. The consistency of the resulting paint may be varied within wide limits by dilution with water without altering its stability; it can therefore be applied by brushing, spraying or printing. Titanium oxide may be used in place of iron oxide and it is also possible to mix the emulsified resin with an aqueous solution containing casein, 2 parts, ammonia, 0.1 part, and chromium oxide, 100 parts. The emulsion of the alkyd resin may be mixed with 20 parts of the azo dye pigment Lithol Red [B] (prepared from diazotized 2-naphthylamine-1-sulphonic acid and  $\beta$ -naphthol) and 80 parts of chalk.

One hundred parts of a hard condensation product from 276 parts of glycerol, 278 parts of linoleic acid and 518 parts of phthalic anhydride can be dissolved in a mixture of 90 parts of toluene and 10 parts of alcohol and then admixed with an emulsion consisting of 50 parts of shellac wax saponified by aqueous ammonia, 10 parts in 240. Further incorporation of 100 parts of yellow iron hydroxide yields a paint when diluted with water prior to application.

These paints can be applied in the manufacture of waterproof wallpapers, it being possible to print by rollers several designs in rapid succession, without the colors flowing into one another. They also have a general application for rendering porous surfaces waterproof. A paint can also be prepared by adding rouge to montan wax saponified by ammonia and mixed with toluene, water and the modified alkyd resin. The modified resin may also be emulsified with an aqueous solution of casein, ammonia and a small amount of a magnesium or lead salt of a high molecular weight organic acid.<sup>13</sup> Compositions for priming or surfacing

<sup>10</sup> W. Baird and H. M. Bunbury, British P. 349,908, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 2071. French P. 708,399, 1930; *Chem. Abs.*, 1932, 26, 1460. For other urea-formaldehyde alkyds, see Chapter 45.

<sup>11</sup> H. J. Barrett and G. L. Dorrough, U. S. P. 1,967,220, July 24, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 6035.

<sup>12</sup> F. Frick, German P. 551,681, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4968. British P. 344,458, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4723. French P. 713,897, 1931; *Chem. Abs.*, 1932, 26, 1811.

<sup>13</sup> F. Frick, German P. 554,721, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 199.

absorbent foundations of stone or wood are furnished by the water emulsions of condensation products from glycerol or pentaerythritol and phthalic, malic or maleic acids together with linoleic or eleostearic acids.<sup>14</sup> If to the aqueous emulsion of linseed oil-modified alkyd are added small amounts of casein, ammonia and a manganese or lead salt of an organic acid, an adherent floor covering can be made.<sup>15</sup> Products obtained by the alkaline neutralization of the synthetic resins, added to make-up water, can also be used in waterproofing concrete.<sup>16</sup>

Suspensions or colloidal solutions of glycerol phthalate resins can be obtained by pulverizing the resin in the B-stage of condensation, screening off the larger particles and mixing the powder with about 10 per cent of a plastic clay, such as natural kaolin. Water is added, and the whole is stirred while being heated to its boiling point.<sup>17</sup> Paper when treated with an aqueous solution of the alkyd resin containing clay can be stacked in layers and molded under heat and pressure to form a laminated product.<sup>18</sup> Moreover, these suspensions may be utilized as adhesives or as binding agents in plastic compositions containing mica, asbestos, wood flour or ground minerals. They are useful for coating surfaces of metal or glass or for the preparation of moldings. Subsequent heat curing is employed in either case. Plastic materials are prepared by neutralizing with volatile bases the intermediate acid products formed during the reaction of polybasic acids with polyhydric alcohols. The neutral products are condensed by heating.<sup>19</sup> Alkyd resins can be combined with amino alcohols which include mono-, di- and triethanolamine, diaminopropanol, butanolamine and pentanolamine. These derivatives can be dispersed in water and the free acidic groups converted into salts. They are said to be particularly useful in making aqueous dispersions of dyes for dyeing and printing textile fibers and for dispersing lakes and pigments for use as aqueous paints.<sup>20</sup>

#### METALLIC SALTS OF RESINS

The soluble products formed from alkyd resins by treatment with aqueous alkalies yield a series of metallic derivatives when treated with solutions of metallic salts (barium or calcium chloride, cobalt nitrate or copper sulphate).<sup>21</sup> For example, on adding a 1 per cent aqueous solution of barium chloride to a 10 per cent aqueous solution of an ammonium glycerol phthalate, an insoluble barium salt is precipitated. It is a white pulverulent solid which is insoluble in common solvents and coheres to give a fairly clear, very hard film on heating at 120°C. A 1 per cent cobalt nitrate solution with ammonium glycerol phthalate yields a pink, fairly flocculent cobalt derivative which forms a clear, hard film on stoving at 100°C. The salt, moreover, is soluble in a mixture of methylated spirits and benzene and is compatible with nitrocellulose. The green copper compound resembles the cobalt derivative in solubility and in hardness. The calcium salt is formed by adding a 5 per cent solution of calcium chloride in methyl alcohol to

<sup>14</sup> British P. 362,479, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1065. See also F. Frick, German P. 552,624, 1928; *Chem. Abs.*, 1932, 26, 5776.

<sup>15</sup> A. Runte and A. Menger, German P. 577,885, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 607.

<sup>16</sup> German P. 560,447, 1930, to A.-G. Johannes Joeserich; *Chem. Abs.*, 1933, 27, 1133.

<sup>17</sup> R. D. Kleeman, British P. 371,637, 1931, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 3629. French P. 716,931, 1931, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 2880. German P. 604,081, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1935, 29, 854.

<sup>18</sup> R. E. Coleman, British P. 398,618, 1932, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1934, 28, 1484.

<sup>19</sup> French P. 723,007, 1931, to Deutsche Gasglühlicht-Auer-G.m.b.H.; *Chem. Abs.*, 1932, 26, 4142. British P. 389,832, 1933; *Chem. Abs.*, 1933, 27, 4640.

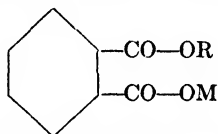
<sup>20</sup> H. Dreyfus, British P. 394,657, 1933; *Chem. Abs.*, 1934, 28, 272.

<sup>21</sup> W. Baird, British P. 357,125, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 26, 4736. French P. 719,655, 1931; *Chem. Abs.*, 1932, 26, 3946.

a 20 per cent methanol solution of the potassium salt of a glycerol phthalate resin. The properties of the metallic derivative depend on the resin ingredients. The cobalt compound of a glycerol phthalate condensation product of acid value 126 is virtually insoluble in a toluene-methyl alcohol mixture. The cobalt derivative of the castor oil-modified glycerol phthalate is quite soluble in this solvent. These metallic products may be used in conjunction with fillers and other natural or synthetic resins for the production of molded materials and for impregnating porous bodies.

Alkaline solutions of alkyd resins with an acid number of not less than 100 react with alkyl or aralkyl halides to give resinous products which are compatible with cellulose derivatives. Propyl iodide, for example, may be added to the potassium derivative of a glycerol phthalate resin dissolved in glycol monoethyl ether, and, after heating, the mixture is filtered and evaporated to give a resin which is finally washed with water and dried.<sup>22</sup>

A monoalkyl ester of phthalic acid is readily prepared by heating phthalic acid with an alkylating agent in molecular proportions. The ester is purified by dissolving in sodium carbonate, extracting any dialkyl phthalate with ether and precipitating the monoalkyl ester with acid.<sup>23</sup> By replacing one acidic hydrogen atom of phthalic acid by a metallic atom and the second by an alkyl or aryl radical, compounds are obtained which are soluble in many organic solvents such as ether and acetone. The derivatives furnish a good method of introducing the heavy metals into mixtures as drying agents in paints and varnishes<sup>24</sup> and to reduce the transmission of ultraviolet light.<sup>25</sup> Compounds of the general type



R = alkyl or aryl; M = heavy metal

are readily prepared by mixing an aqueous solution of the sodium salt of the monoalkyl phthalic ester with a solution of a soluble salt of a heavy metal (iron, zinc, manganese, tin, lead, mercury, copper or cobalt). The metal phthalic ester is precipitated in this way. The ferrous and ferric neutral salts of monophthalic esters such as the n-butyl ester are brownish red in color, whereas the zinc, mercurous, mercuric, plumbous and stannous salts are colorless. The manganous and nickel salts are green; the cobaltous and cupric salts are blue. All of the compounds are formed initially as viscous oils, except the copper and manganese salts, which are crystalline at room temperature. These substances simulate those formed directly from solutions of alkyd resins in alkalies.

Metallic derivatives of this type readily form colloids with nitrocellulose. Thus, a nitrocellulose film may be prepared from 10 parts of pyroxylin, 5 parts of zinc n-butyl phthalate and a volatile solvent. The pyroxylin and zinc salt are rendered colloidal in the same way as pyroxylin and camphor would be, the volatile solvent being added to give the required consistency. Films prepared in this manner are uniform and transparent. A non-opaque coating com-

<sup>22</sup> W. Baird and R. Hill, British P. 362,972, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 1531.

<sup>23</sup> E. R. Littmann, B. K. Brown and W. J. Bannister, British P. 250,265, 1925, to Commercial Solvents Corp.; *Brit. Chem. Abs. B*, 1927, 532. Canadian P. 260,928, 1926; *Chem. Abs.*, 1926, 20, 2504.

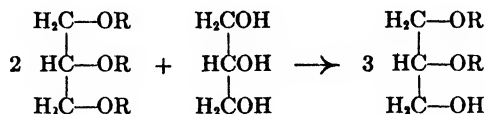
<sup>24</sup> C. I. B. Henning, C. E. Burke and E. E. Reid, U. S. P. 1,742,506, 1,742,507 and 1,742,508, Jan. 7, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 24, 1122, 1235.

<sup>25</sup> F. L. Salzberg, U. S. P. 1,965,608, July 10, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 5667.

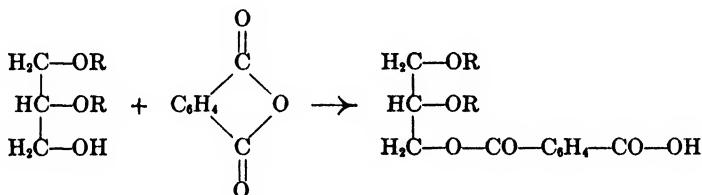
position consists of cellulose nitrate, pearl essence and a salt (iron, copper, cobalt, nickel or manganese) of the half-acid ester of a dibasic acid.<sup>26</sup>

Cobalt butyl phthalate will serve as a drier in varnish inasmuch as it is very soluble in turpentine and oils. An example of a varnish containing this drier consists of tung oil, 50 gals., linseed oil, 12.5 gals., rosin, 120 lbs., turpentine, 125 gals. and cobalt butyl phthalate, 1.22 lbs. Other heavy metal salts of the hemi-alkyl esters may be used in place of the cobalt derivative. Metal alkyl phthalates together with rubber, oils and cellulose derivatives yield a composition which, dissolved in benzene or carbon disulphide, can be used as an adhesive on moisture-proof regenerated cellulose.<sup>27</sup>

By reacting two mols of vegetable oil with one mol of glycerol, the tendency is toward the formation of the diglyceride. The reaction may be expressed as follows:



Reacting the diglyceride with phthalic anhydride, results in the formation of the half-acid ester.



For example 620 g. of linseed oil and 31 g. of glycerol are heated for 30 minutes at 250°C. in the presence of litharge or alkali which serves as a catalyst. The resulting linseed diglyceride is esterified with 148 g. of phthalic anhydride by heating for 30 minutes at 140°C. to yield the phthalic half-acid ester of linseed diglyceride. This product when dissolved in alcohol, neutralized with alkali and treated with a heavy metal salt yields the corresponding derivative. The incorporation of the latter into alkyd resins reduces the transparency to ultraviolet light. The ferric, copper, cobalt, vanadium, cerium and titanium derivatives are effective. The iron compound has a greater retarding value for ultraviolet light than titanium but the iron colors the film. Combination of both metal salts results in the desired opacity and the minimum coloration.<sup>28</sup>

Brown and Bogin<sup>29</sup> have contributed largely to the development of metal alkyl phthalates for use in cellulose acetate compositions. According to these investigators, the addition of varnish gums (dammar, kauri, shellac) to nitro-cellulose lacquers adds body, covering power, adherence and durability without increasing the viscosity. The use of cellulose acetate in lacquers has been limited by incompatibility of many resins and cellulose acetate. Even though the components

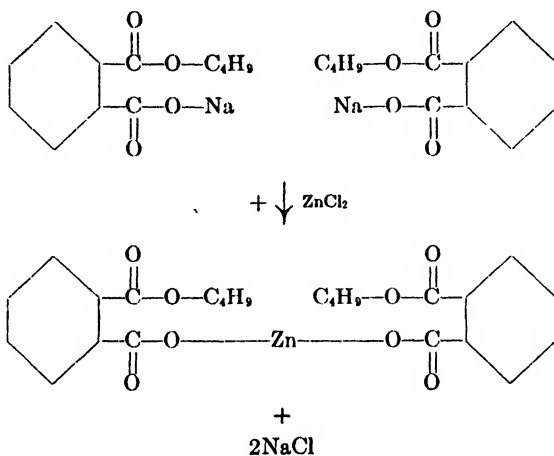
<sup>26</sup> G. R. Enslinger, U. S. P. 1,939,676, Dec. 19, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1557.

<sup>27</sup> E. B. Bengel, U. S. P. 1,953,946, Apr. 10, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1935, 163.

<sup>28</sup> P. L. Salsberg, U. S. P. 1,980,441, Nov. 13, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 255. Canadian P. 333,043, 1933, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 4423. British P. 381,163, 1931; *Brit. Chem. Abs.* B, 1933, 1091. See also H. Bradshaw, Canadian P. 325,468, 1929, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 25, 4486.

<sup>29</sup> E. K. Brown and C. Bogin, U. S. P. 1,591,653, July 6, 1926, to Commercial Solvents Corp.; *Brit. Chem. Abs.* B, 1926, 753. Canadian P. 290,927, 1926; *Chem. Abs.*, 1926, 20, 2584. German P. 506,957, 1925; *Chem. Abs.*, 1931, 25, 536.

might be dissolved in a liquid without precipitation taking place, the evaporation of the solvent results in the formation of a fogged film. This drawback is not shown by the polyvalent metallic salts of the half esters of phthalic acid. The following equation illustrates the method of forming the compounds:



Phthalic anhydride and butyl alcohol are heated in toluene at 100°C. until the butyl acid phthalate is formed. The solution is neutralized with sodium hydroxide until alkaline to phenolphthalein and then zinc sulphate is added. The resin is freed from solvent and water by distillation below 80°C. Alternatively the alkyl hydrogen phthalate is treated directly with zinc oxide in presence of an organic solvent.<sup>30</sup> The zinc salt of the monobutyl ester of phthalic acid is described as a friable, transparent, gum-like material which is hard enough at room temperature so that it may be pulverized like hard rosin. It softens with increasing temperature to become liquid at 150°C.

Brown and Bogin's<sup>31</sup> method of using these salts to prepare a cellulose acetate-resin lacquer is illustrated by the following example: To 16 oz. of acetone-soluble cellulose acetate dissolved in 2 qts. of a solvent mixture composed of 80 per cent of a low-boiling cellulose acetate solvent (acetone) and 20 per cent of a higher-boiling solvent (diacetone alcohol or tetrachloroethane), 16 oz. of ferric or copper alkyl resin dissolved in 2 qts. of an identical phthalate mixture are added. Frequently it is desirable to add a plasticizer to produce a more elastic or extensible film; dibutyl phthalate may be employed in the solution in amounts up to 100 per cent of the weight of cellulose acetate.<sup>32</sup> The normal monobutyl esters of phthalic acid are said to yield the best resins.

By grinding a pigment in the presence of a liquid ester of phthalic acid (dibutyl phthalate) and a metal salt of the hemi-acid ester of phthalic acid (zinc, copper, iron or aluminum butyl phthalate) a product is formed for use in nitrocellulose enamels. Alternatively, the pigment may be ground in presence of tritoyl phosphate and a metal salt of the hemi-acid ester of phthalic acid.<sup>33</sup> Compounds such as sodium butyl glycerol phthalate, which is formed when part of the free carboxyl group in glycerol phthalate is esterified with a monohydric alcohol and the

<sup>30</sup> W. J. Bannister, U. S. P. 1,779,654 and 1,779,688, Oct. 28, 1930, to Commercial Solvents Corp.; *Brit. Chem. Abs.* B, 1931, 669.

<sup>31</sup> B. K. Brown and C. Bogin, *loc. cit.*

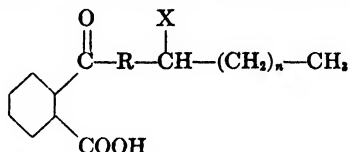
<sup>32</sup> A. R. Littmann, B. K. Brown and W. J. Bannister, British P. 250,265, 1925; *Chem. Abs.*, 1927, 21, 1031. Canadian P. 269,923, 1926; *Chem. Abs.*, 1926, 20, 2504.

<sup>33</sup> C. W. Simons, W. J. Bannister, L. C. Swallen, U. S. P. 1,864,151 and 1,864,152, June 21, 1932, to Commercial Solvents Corp.; *Chem. Abs.*, 1932, 26, 4486.



remainder of the acid is converted into a salt, together with the corresponding zinc, calcium and copper salts, as well as zinc isoamyl glycerol phthalate, may be used for plasticizing cellulose esters and as components of other synthetic resins.<sup>44</sup> A nitrocellulose coating containing these salts reduces the transmission of ultra-violet light.

Bruson<sup>45</sup> found that polyvalent metal salts of organic acids of the type



"n," whole number greater than unity

"X," hydrogen or alkyl group

"R," an aromatic nucleus

have the property of dissolving in raw linseed, tung, soya-bean and related oils, as well as in turpentine, solvent naphtha, mineral spirits, gasoline and in oil varnishes and paints. Examples of this type of substance are *n*-butylbenzoyl-*o*-benzoic acid, sec-amyl-naphthoyl-*o*-benzoic acid and sec-octyltoluyl-*o*-benzoic acid. Salts of these acids may be incorporated readily in large proportions in such oil compositions as linoleum, printing inks, oil enamels, varnishes and the like and appear to be particularly stable at low temperatures and under varying conditions of dilution and of oil viscosity. They function as siccatives, hardening agents or gloss promoters. When used as siccatives in oil enamels, they do not produce livering or thickening with basic pigments and show little tendency to "after-yellowing" in white enamels.

One example is as follows: to 145 g. of phthalic anhydride in 740 g. of sec-amylbenzene, in a vessel fitted with an agitator, are added 296 g. of anhydrous aluminum chloride in small portions so that the temperature of the reacting mass does not exceed 25°C. The mixture is then stirred continuously for 4 to 5 hours and is next warmed to 45°C. for 5 hours. The dark brown reaction product is decomposed with ice water or with hot soda solution. The latter procedure allows the alumina which forms to be filtered off, that is, after the mixture has been steam distilled to remove unreacted hydrocarbon. The filtrate is then acidified with dilute sulphuric acid and the sec-amylbenzoyl-*o*-benzoic acid separates as a waxy mass which need not be purified for the second step of the preparation.

After washing, the crude waxy acid is carefully neutralized with a 10 per cent sodium hydroxide solution until faintly pink to phenolphthalein and is then treated with a slight excess of a 20 per cent aqueous solution of a water-soluble salt. Cobalt sulphate, manganous chloride, plumbous nitrate, aluminum sulphate or copper sulphate and the like can be used. The metal salts precipitate out as amorphous masses, which are purified by dissolving in an organic solvent (toluene, ethylene dichloride or acetone), filtering and finally evaporating off the solvent. The aluminum, barium, calcium, lead, cerium, magnesium, strontium and zinc salts of sec-amylbenzoyl-*o*-benzoic acid are white, whereas the chromium, cobalt, copper, iron and vanadium salts are colored. The metal salt is usually dissolved in an appropriate solvent before incorporation in the varnish, paint or printing material. Oils or varnishes of the linseed oil type when mixed with the above cobalt, manganese or vanadium salts corresponding to 0.05 per cent metal to the weight of oil show a decrease in the drying time from 24 hours to approximately 6 hours.

A satisfactory amylbenzene for the above reaction is obtained by condensing amyl alcohol with benzene in presence of a dehydration catalyst (concentrated sulphuric acid or zinc chloride). As the length of the chain of the alkyl substituent in the benzene, toluene, xylene or naphthalene nucleus is increased, the oil-solubility of the polyvalent salts increases.

<sup>44</sup> L. C. Swallen and W. J. Bannister, U. S. P. 1,835,915, Dec. 8, 1932, to Commercial Solvents Corp.; *Chem. Abs.*, 1933, 26, 696.

<sup>45</sup> H. A. Bruson, U. S. P. 1,934,033, Nov. 7, 1933, to Resinous Products & Chemical Co., Inc.

Nitrophthalic acid has been substituted for phthalic acid in alkyd resins. The manufacture of 3-nitrophthalic acid in such a way as to avoid losses due to higher nitration products may be carried out as follows:<sup>36</sup> 185 lbs. of phthalic anhydride are agitated with 248 lbs. of concentrated nitric acid (sp. gr. 1.42), to which 322 lbs. of sulphuric acid (sp. gr. 1.84) are slowly added. The mixture is maintained at 95°C. until the reaction is completed, and then cooled to 50-60°C. and run into 500 lbs. of water. After mixing well, the 3-nitrophthalic acid is collected by centrifuging or filtration. Traces of water or nitric acid are removed by agitation with 600 lbs. of benzene and then distilling off the water and nitrobenzene. The remaining benzene is removed either by filtration or by vacuum distillation. The yield is 85-90 per cent based on phthalic anhydride.

The half esters of nitrophthalic acid may be prepared by reacting one mol of an aliphatic or aromatic alcohol with 1 mol of nitrophthalic acid, using a catalyst such as a mineral acid.<sup>37</sup> These half esters resemble phthalic acid in that they will readily form soluble sodium and potassium salts on treating with aqueous alkali. The sodium derivatives give insoluble compounds when mixed with solutions containing salts of heavy metals. The heavy-metal products, although they are insoluble in water, dissolve in many organic solvents. These substances are resin-like in appearance and properties, and may serve as substitutes for natural gums or resins. The zinc, tin and lead compounds are colorless; nickel, chromium and copper are greenish blue whereas iron, cobalt and manganese are reddish derivatives.

#### MISCELLANEOUS COMPOSITIONS AND APPLICATIONS

The reaction of half-esters of dicarboxylic acids with amines yields products such as aniline butyl phthalate, naphthylamine ethyl phthalate or monobutylamine butyl phthalate.<sup>38</sup> The last-named compound is a colorless transparent syrupy liquid, decomposing about 150°C. and soluble in water, methyl or ethyl alcohol, benzene, acetone or ether.

In the production of photographic films, the anti-halation layer can be protected by a thin coating of a non-aqueous solution of a natural or synthetic resin containing at least one hydroxyl or carboxyl group capable of forming a water-soluble alkali salt.<sup>39</sup> An emulsion containing glycerol phthalic acid condensation products, toluene, gelatin, soap and water, with oil or wax if desired, can be used in impregnating paper for producing a waterproof and insulating material. After impregnation, the paper is dipped in an alum or formaldehyde bath.<sup>40</sup> Smooth paper with a high luster and good printing properties is obtained by mixing paper pulp with a small proportion of a metal salt of an acid ester, such as barium monocetyl phthalate. A binder (casein or gelatin) may also be added.<sup>41</sup>

The condensation products from polybasic acids and polyhydric alcohols, either in solution or in the form of an emulsion, may be added to aqueous solutions of water-soluble alkyl cellulose derivatives (as methyl cellulose). The mixture is then subjected, either during or after removal of water, to heat or to exposure to light of short wave length, films or filaments being thus obtained.<sup>42</sup>

<sup>36</sup> E. R. Littmann, U. S. P. 1,549,385, Aug. 18, 1925, to Commercial Solvents Corp.

<sup>37</sup> E. R. Littmann, U. S. P. 1,618,209, Feb. 22, 1927, to Commercial Solvents Corp.; *Brit. Chem. Abs.*, B, 1927, 340.

<sup>38</sup> W. J. Bannister, U. S. P. 1,803,298, April 28, 1931, to Commercial Solvents Corp.; *Chem. Abs.*, 1931, 25, 3665.

<sup>39</sup> French P. 747,530, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5015. *British P.* 397,740; *Brit. Chem. Abs.*, B, 1933, 940.

<sup>40</sup> *British P.* 391,350, 1933, to Knaggs, Marsden & Portals, Ltd.; *Chem. Abs.*, 1933, 27, 4925.

<sup>41</sup> W. Weiss and E. Metzger, German P. 557,337, 1930, to Zschimmer & Schwarz Chem. Fabr.; *Chem. Abs.*, 1933, 27, 418.

<sup>42</sup> *British P.* 308,384, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 239.

## Chapter 47

### Alkyd Resins. Uses in Coatings

It is well known that nitrocellulose solutions give hard quick-drying films. In the development of lacquers employing cellulose esters it was noted that improvements in gloss, adhesion and durability were secured by incorporation of limited amounts of natural resins. Later observations showed that unusual improvements resulted when synthetic resins were employed.

Synthetic resins of the alkyd type have proved themselves preëminently adaptable for use in the preparation of coating materials. As will be seen in the following pages they are frequently utilized as the sole binding agent. They also find very extensive application in conjunction with nitrocellulose. As a preliminary to the discussion of the actual application of alkyd resins for coatings, some consideration must necessarily be given to the general properties and uses of such coatings and to tests which have been made to determine their weathering qualities.

#### GENERAL PROPERTIES OF ALKYD RESIN COATINGS

Synthetic resins<sup>1</sup> of the glycerol phthalate type are now manufactured under several trade names such as "Glyptal,"<sup>2</sup> "Rezyl,"<sup>3</sup> "Teglac,"<sup>4</sup> "Alkydal," and "Dulux";<sup>5</sup> variations in properties being made according to the purpose for which the finished product is to be utilized.

Glyptal lacquers<sup>6</sup> are resistant to all the heavier mineral oils and, after baking, will also resist such substances as gasoline and kerosene.<sup>7</sup> They are unattacked by weak acids and alkalies, and will withstand temperatures of 300°C. They are adaptable to the covering of metallic surfaces (aluminum or galvanized iron) which are normally difficult to coat. A tenacious adhesion is, in fact, one of the outstanding properties of these lacquers, and they produce finishes which are smooth, readily cleaned and, as a rule, resistant to abrasion. These lacquers are applied by spraying, brushing or dipping; they air-dry in 30 minutes, may be handled in 2 hours and will set hard in from 8-10 hours. The drying time is greatly accelerated by heat.<sup>8</sup>

<sup>1</sup> For a review of the use of synthetic resins in lacquers see R. C. Martin, *Metal Cleaning and Finishing*, 1933, 5, 203, 251; *Chem. Abs.*, 1933, 27, 3349, 4425. H. Külln, *Farbe u. Lack*, 1935, 30, 51; *Chem. Abs.*, 1935, 29, 3180. W. Krumbhaar, *Verfkronek*, 1935, 8, 13; *Chem. Abs.*, 1935, 29, 3374. R. Dittmar, *Caoutchouc et gutta-percha*, 1935, 32, 17097, 17131; *Chem. Abs.*, 1935, 29, 3419. E. Fonrobert, *Verfkronek*, 1934, 7, 333; *Chem. Abs.*, 1935, 29, 3180.

<sup>2</sup> The Glyptal resins are a product of the General Electric Co.

<sup>3</sup> The Rezyls and Teglaes are products of the American Cyanamid Co.

<sup>4</sup> Alkydal resins are manufactured by the I. G. Farbenindustrie A.-G.

<sup>5</sup> Dulux was developed by the E. I. du Pont de Nemours & Co. and manufactured also by the Nobel Chemical Finishers, Ltd. (Imperial Chem. Ind., Ltd.).

<sup>6</sup> L. E. Barringer, *General Electric Rev.*, 1929, 32 (12), 660; *Chem. Abs.*, 1930, 24, 1224.

<sup>7</sup> J. McE. Sanderson (*Paint, Oil, Chem. Rev.*, 1932, 95 (11), 38; *Chem. Abs.*, 1933, 27, 3635) has discussed the considerations governing the selection of solvents for alkyd solutions. See also Beck, Koller & Co., *Paint, Oil, Chem. Rev.*, 1934, 96 (10), 18; *Chem. Abs.*, 1934, 28, 4234 for observations concerning the solubility of alkyds with respect to the tolerances of a number of resin solutions for denaturated alcohol, ethyl acetate and mineral spirits, and W. J. Sweeney and J. A. Tilton, (*Ind. Eng. Chem.*, 1934, 26, 693) for hydrogenated naphthas as solvents for alkyd resins. For the use of a hydrogenated petroleum oil (Hydrosolvent) as a solvent for drying oil alkyds, see W. H. Wright, U. S. P. 1,977,000, Oct. 23, 1934, to Schenectady Varnish Co., Inc.; *Chem. Abs.*, 1935, 29, 306.

<sup>8</sup> The kinetics of the baking process of oil varnishes has been studied by R. H. Kieule (*Ind. Eng. Chem.*, 1930, 22, 1370).

Teglacs, although originally developed for use in lacquers, are now finding prominence in both varnishes and enamels. They are essentially phthalic glycerides modified with natural resin acids. Certain of the Teglacs provide a better combination of hardness and toughness than is secured by ester gum. In lacquer enamels they do not impart durability to the extent of the Rezyls, so that they find application chiefly in the sphere of indoor finishes, especially in clear furniture lacquers where hardness and high refractive index impart wearing qualities and high gloss. They are not readily soluble in oils, but dissolve easily in cold toluene, in Cellosolve or in petroleum distillates. They are hard and have a low solvent retention, so that they rub well and are well adapted for use in lacquer sanding sealers.

The Rezyls fall into two classes depending upon whether saturated or unsaturated acids enter into their composition. The saturated Rezyls, also known as the lacquer type of Rezyls, may further be sub-classified as to their compatibility with cellulose acetate or nitrocellulose. The application of the saturated Rezyls in lacquers depends largely on their stability to ultraviolet light and to their retention of gloss and color on exposure to weather. They have, accordingly, been largely used in pigmented lacquers for automobiles, and in architectural brushing lacquers. They have also been used in the production of clear lacquers for bright metal hardware. Because of toughness, color-retention and good solubility, a comparatively low proportion of nitrocellulose is necessary. Rezyls of this type are produced industrially in the form of pale-colored viscous liquids or solid resins softening at 60-69°C., the acid number varying from about 20-35 according to type. They are completely miscible with nitrocellulose and compatible with other lacquer resins, so may be worked in almost any formulation of materials without difficulty. They are soluble in toluene or xylene, or in some cases better, in toluene- (or xylene)-ethyl acetate or butyl acetate mixtures. Dissolved in medium- or high-boiling solvents, they may be used as the vehicle for grinding pigments. Highly basic pigments, such as zinc oxide, are not recommended by the manufacturers for use with these resins.

The unsaturated oxidizing Rezyls are used to some extent in lacquers but find their most extensive application as binders by themselves or in combination with drying oils and resins. They find a wide variety of uses among which can be mentioned drum enamels, freight car paint, house paint, white baking enamel, truck enamels, sign finishes, auto undercoats and printing inks.\* Further treatment of this type of resin as a coating material will be deferred to the following chapter.

There is also a series of high-acid Rezyls for use in aqueous ammonia solutions. The "Ellisols" are a related series of ammonia-water-soluble resins which find application in the impregnation of paper and cloth.<sup>10</sup>

The Alkydal resins<sup>11</sup> are free of natural resin (show no Storch-Morawski reaction) and contain, moreover, no free fatty oils. The absence of phenols enhances their resistance to the action of light. Various grades of quick-drying and baking compounds are produced, which may supplant the usual drying oils or may be admixed with nitrocellulose. The air-drying Alkydals may be somewhat modified by incorporation of small amounts of other natural or synthetic resins, or ester gums; they may be used with any of the usual inorganic pigments, although the use of zinc oxide requires careful formulation on account of the acid number (20-30). The baking Alkydals are designed to dry at 100-

\* J. McE. Sanderson, *Paint, Oil, Chem. Rev.*, 1934, 96 (12), 11; *Plastic Products*, 1934, 10, 141. H. Chase, *Elec. Mfg.*, 1934, 14 (1), 23; *Chem. Abs.*, 1934, 28, 5690.

<sup>10</sup> See Chapter 48.

<sup>11</sup> For tests with Alkydal resins see H. Wolff and B. Rosen, *Farben-Ztg.*, 1933, 36, 1020; *Brit. Chem. Abs. B.*, 1933, 676.

120°C. in one-half to one hour, the addition of about 10 per cent of natural (e.g., dammar) or synthetic resins assists rapid baking and minimizes the tendency to wrinkling found in viscous enamels. Phenolic resins are said to be unsuited for incorporation in this way. Cobalt driers may be added to produce wrinkled and frosted finishes. Alkydals are compatible with nitrocellulose, producing finishes of a high gloss, and particularly free from chalking, which are not, however, suited for sanding and rubbing. The Alkydals may be admixed with drying oils.

Dulux is a drying oil-modified glycerol phthalate resin of extreme hardness and elasticity and permits rigorous treatment of the coated article without flaking or cracking of the film. This will also be treated in a subsequent chapter.

#### DETECTION OF PHTHALATE TYPE RESINS

The density of glycerol phthalate varies from 1.33-1.42, and that of ethylene glycol phthalate from 1.31-1.36; the refractive indices in each case being about 1.56-1.58. Heated in a Pyrex tube over a free flame a phthalate resin will give a white sublimate of phthalic anhydride which can be identified by its reaction with resorcinol to form fluorescein.<sup>12</sup> Scheiber<sup>13</sup> recommends the procedure of heating resorcinol and sulphuric acid with the alkyd resin whereas Cannegieter<sup>14</sup> is in favor of omitting the acid, inasmuch as it leads to charring. A more accurate method<sup>15</sup> involves refluxing the resin in the presence of benzene and alcoholic potash. After distilling off the benzene and alcohol, the unsaponifiable matter is extracted with ether, acidified with hydrochloric acid and further extracted with benzene. The phthalic acid is then precipitated with lead acetate in faintly alkaline solution and the precipitated lead phthalate converted to lead sulphate and weighed.

Apart from qualitative tests, which are reliable methods of detecting phthalates in a coating composition, data relating to specific gravity, refractive index, saponification number, nature of saponifiable matter and melting point may all be applied in the examination of supposed alkyd resins.<sup>16</sup>

#### EXPOSURE TESTS WITH ALKYD RESINS

Gamble and Stutz<sup>17</sup> have studied the light-transmission characteristics of a number of synthetic resins (see Fig. 128). The glycerol phthalate resins were found to be fairly transparent at wave lengths greater than 3000Å.<sup>18</sup> The resins

<sup>12</sup> T. F. Bradley (*Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 308) has worked out qualitative tests for the detection of phthalate resins. The resorcinol test is as follows: "Heat from 0.25 to 1 g. of the resin in a test tube with from 2 to 3 times this amount of pure resorcinol to the boiling point of the resorcinol (205° to 210°C.) for several minutes. Cool and extract with boiling water with agitation of the fused mass. Dilute to from 50 to 100 cc. with distilled water. Render slightly alkaline with dilute aqueous sodium hydroxide solution, when, in the event that phthalates are present, a typical greenish yellow fluorescence of fluorescein will result." The test is also applicable to the sublimate (0.05 g. or more) which may be formed on strong fusion of the resin. It is applicable to the detection of phthalate plasticisers in lacquers.

The phenol test is carried out in the following manner: "A less sensitive but useful confirming test involves the treatment of the resin (or other form of phthalate) with phenol and a condensing agent to form phenolphthalein. Heat 1 gram of the resin with from 2 to 3 times this amount of pure phenol and 10 drops of concentrated sulphuric acid in a test tube over an open flame until visible reaction occurs with formation of an orange or brownish orange melt. Avoid undue charring of the resin by limiting the amount of sulphuric acid and the time and temperature of the operation. After cooling the melt somewhat, extract it with boiling water, with agitation, dilute to 100 cc., and render slightly alkaline with aqueous sodium hydroxide solution. The typical pink of phenolphthalein as exhibited in alkaline solutions is a positive test for phthalates."

<sup>13</sup> J. Scheiber, *Farbe u. Lack*, 1933, 592; *Brit. Chem. Abs. B*, 1934, 156.

<sup>14</sup> D. Cannegieter, *Verfahrenstechnik*, 1934, 7, 256; *Chem. Abs.*, 1935, 29, 3003.

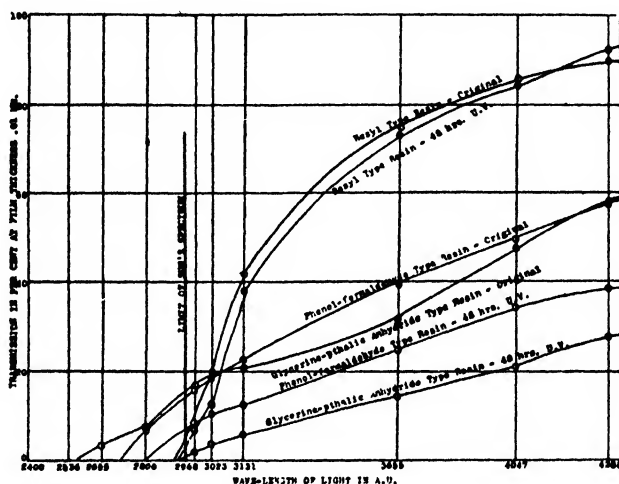
<sup>15</sup> H. Ulrich, *Farbe u. Lack*, 1934, 318; *Brit. Chem. Abs. B*, 1934, 804.

<sup>16</sup> See Chapter 64.

<sup>17</sup> D. L. Gamble and G. F. A. Stutz, *Ind. Eng. Chem.*, 1929, 21, 330.

<sup>18</sup> A filter opaque to rays of wave length greater than 3900 Å is formed from a cellulose derivative

made with glycol, and also the glycerol-phthalic anhydride-oil resins had about the same transparency. Kraus<sup>10</sup> examined the degree of yellowing when various resins and plasticizers were exposed to ultraviolet light separately and in admixture with nitrocellulose. The degree of yellowing was not additive, but was always greater than the sum of the individual yellowing effects, indicating that the effect is due, in part, to reactions among the components of the lacquer. Especially good light-resistance was shown by lacquers containing glycerol phthalate, according to Kraus. Of the synthetic resins, alkyds in conjunction with diamyl phthalate gave the best weather-resistance.<sup>20</sup>



Courtesy Industrial and Engineering Chemistry

FIG. 128.—Ultraviolet Light Transmission Characteristics of Some Synthetic Resins. (D. L. Gamble and G. F. A. Stutz.)

Experiments conducted by Brendel<sup>21</sup> showed that nitrocellulose lacquers containing alkyd resins remained almost intact after 7 months outdoor exposure. The durability of films containing this type of resin was not a function of the viscosity of the nitrocellulose, a comparatively low proportion of which should be used. The exceptional durability, quick-drying and highly water-resistant surfaces offered by compositions containing nitrocellulose and phthalic anhydride-glycerol resins have led to their adoption under exacting conditions such as those which arise in aircraft manufacture.<sup>22</sup>

Gardner<sup>23</sup> has carried out tests with varnishes containing alkyd resins exposed to salt-water air. A lacquer containing equal parts by weight of nitrocellulose and glycerol phthalate-plasticized resin failed in 9 days after application of one flow coat. The steel under the film showed very slight rust. This lacquer was better than a combination phenolic-phthalic anhydride glycerol ester-tung oil varnish tested under the same conditions. The protection afforded against the

containing sodium benzoate, phthalic anhydride and potassium acid phthalate, according to R. B. Withrow, U. S. P. 1,933,734, Dec. 12, 1933, to General Development Lab., Inc.; *Brit. Chem. Abs. B*, 1934, 909.

<sup>10</sup> A. Kraus, *Farbe u. Lack*, 1930, 206, 221; *Chem. Abs.*, 1930, 24, 4174.

<sup>20</sup> A. Kraus, *Farben-Ztg.*, 1934, 39, 1193, 1241; *Chem. Abs.*, 1935, 29, 1368. See P. H. Faucett, *Drugs, Oils and Paints*, 1934, 49, 453; *Brit. Chem. Abs. B*, 1935, 319.

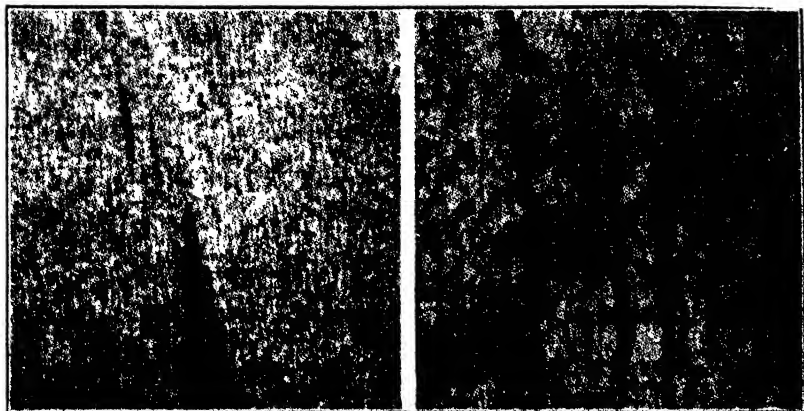
<sup>21</sup> H. Brendel, *Farben-Chem.*, 1933, 3, 130; *Brit. Chem. Abs. B*, 1933, 618.

<sup>22</sup> H. A. Gardner, *Proc. Am. Soc. Testing Materials*, 1930, (30), 37; *Chem. Abs.*, 1931, 25, 1690.

<sup>23</sup> H. A. Gardner, *Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 94; *Circ., Sci. Sec. Education Bureau, Am. Paint, Varnish Mfrs. Assoc.*, 1933, 339, 673; *Chem. Abs.*, 1929, 23, 292.

rusting of steel, for sub-sea-water service, was tested by exposure at 45° inclination during the day and immersion in 3 per cent sodium chloride during the night for six months. Addition of alkyd resin to linseed oil paints and reduction of pigment concentration was without advantage save in the case of the basic lead chromate paints.<sup>24</sup> Other tests on spar, semi-spar and rubbing lacquers again emphasize the superior weathering properties of compositions containing alkyd resins (see Fig. 129). A number of Rezyls were employed in these tests.<sup>25</sup>

Van Heuckeroth<sup>26</sup> has examined the effect of various plasticizers used in a series of lacquers submitted to exposure. A lacquer containing Rezyl<sup>27</sup> gave the best results on red cedar and (in other exposure tests) on metals previously coated with various primers. Alkyd-type primers were found to be superior



Courtesy American Cyanamid & Chemical Corporation

FIG. 129.—Comparative Durability of a Rezyl Lacquer (left) and an Oleo-Resinous Spar Varnish Exposed under Identical Conditions.

to the oleo-resinous variety. Bolme<sup>28</sup> also carried out exposure tests on nitrocellulose lacquers and alkyds, using various accelerated weathering devices. Gettens<sup>29</sup> found that alkyd resins have a low moisture-permeability and, on this basis, are useful in coating materials for the protection of works of art. The durability of a lacquer coating is found to increase with the Rezyl content, which is not the case with other resins. For exterior clear finishing lacquers of great durability on both wood and metal surfaces, three to four parts of Rezyl to one part by weight of nitrocellulose gave good results. For automobile and furniture lacquers more nitrocellulose should be incorporated. Kolke,<sup>30</sup> in a study of the weathering tests of nitrocellulose lacquers on wood, emphasizes the fact that by using appropriate ground coats alkyd resins improve the coating. As shown by exposure tests, pigments have a definite effect on the durability of the paints prepared from drying-oil alkyds and bodied linseed oil.<sup>31</sup> A glaze for walls and tiles said to be resistant to weather and acids is produced by applying in the

<sup>24</sup> H. A. Gardner and G. G. Sward, *Am. Paint, Varnish Mfrs. Assoc.*, 1932, 417, 263; *Brit. Chem. Abs. B*, 1933, 976.

<sup>25</sup> A. W. Van Heuckeroth and H. A. Gardner, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 358, 47; *Brit. Chem. Abs. B*, 1930, 622.

<sup>26</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1931, 399, 377; *Brit. Chem. Abs. B*, 1932, 153.

<sup>27</sup> Rezyl No. 19 and Rezyl balsam No. 33.

<sup>28</sup> S. Bolme, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1931, 404, 2550; *Chem. Abs.*, 1932, 26, 1188.

<sup>29</sup> R. J. Gettens, *Tech. Studies Field Fine Arts*, 1932, 1, 63; *Chem. Abs.*, 1933, 27, 433.

<sup>30</sup> F. Kolke, *Nitrocellulose*, 1932, 4, 200; *Chem. Abs.*, 1934, 28, 1554.

<sup>31</sup> E. A. Bevan and F. J. Siddle, *Paint, Varnish Prod. Mgr.*, 1934, 28.

cold a mixture of quartz, Sorel cement, magnesium sulphate and nitrocellulose, then applying a further coat of nitrocellulose and glycerol phthalate resin and a final hardening lacquer containing acetyl cellulose.<sup>23</sup>

#### ALKYD RESIN COATINGS ON METALS

The alkyd resins find one of their most promising fields of application in the coating and protection of metal surfaces.<sup>23a</sup> One method of utilizing the resin is as an ingredient of a paint consisting of finely divided aluminum suspended in a volatile solvent in which the resin (from an equimolecular mixture of glycerol and phthalic anhydride) has been dissolved. The metal (iron, steel or copper) is coated with this paint, the solvent is allowed to evaporate, and the metal is heated to 380°C. to volatilize the resin. Final heating is carried out at a still higher temperature to cause the aluminum to diffuse into the surface layers of the metal.<sup>23</sup> Metal powders other than aluminum may be used; zinc, copper alloys, silver and gold powders have been suspended in a solvent consisting of butyl alcohol, toluene and naphtha with an alkyd resin modified with drying oils and drying oil acids together with a small percentage of rosin. Paints containing zinc or aluminum may be applied directly to iron or copper and the zinc and aluminum alloyed by heating.<sup>24</sup>

The chief difficulty which arises in connection with the use of cellulose lacquers on metal surfaces is the fact that such lacquers have a tendency to crack away from the surface to which they have been applied.<sup>25</sup> The disadvantage has been successfully overcome by providing the metal surface with an underlying or priming coating of a resin of the glycerol and phthalic anhydride type.<sup>26</sup> In some cases plasticizing agents (indene, glycol diacetate, diethyl phthalate, anisole, triacetin or tricresyl phosphate) may be introduced with advantage into the resin during its manufacture. A solution of the glycerol phthalate resin in a solvent consisting of 30 parts of acetone, 30 parts of benzene, 30 parts of alcohol and 10 parts of ethyl lactate by volume may be used. Such a solution of 0.925 specific gravity at 60°F. is suitable for spraying. A film produced by spraying is first air-dried and subsequently baked for 20-40 minutes at 125-175°C. Under these conditions, the resin is transformed into the B-stage. The adjustment of time, temperature and other baking conditions must be such as to expel all of the solvent from the lacquer and render the coating non-tacky, but still soft enough to provide the proper anchorage for the cellulose lacquers to be superimposed. When a high-boiling solvent is present some of it will be retained in the baked resin, thereby increasing its flexibility. A cellulose lacquer in a solvent consisting of butyl phthalate, dibutyl phthalate, ethyl lactate, ethyl acetate, glycol diacetate or similar volatilizable material is then applied by spraying. The solvent of the cellulose lacquers softens the underlying resin somewhat and thereby binds the two films together. The time required for baking the resin coating, and also

<sup>23</sup> Swiss P. 167,098, 1934, to A.-G. Internationale Patentverwertung; *Chem. Abs.*, 1935, 29, 570.

<sup>23a</sup> See B. Scheiffe, *Paint. Varnish Prod. Mgr.*, 1935, 12 (June), 14.

<sup>24</sup> J. G. E. Wright, U. S. P. 1,829,623, Oct. 27, 1931, to General Electric Co.; *Chem. Abs.*, 1932, 26, 691. British P. 350,250, 1930, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 265. French P. 706,065, 1930, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 76. German P. 558,674, 1929, to Allgem. Elektricitäts-Ges.; *Chem. Abs.*, 1933, 27, 615.

<sup>25</sup> L. V. Adams, British P. 337,682, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1931, 25, 2310. Canadian P. 313,728, 1931; *Chem. Abs.*, 1931, 25, 5304.

<sup>26</sup> P. W. Ham (*Official Digest, Fed. Paint Varnish Prod. Clubs*, 1934, 135, 102; *Chem. Abs.*, 1934, 28, 3002) in a study of the problem of "lifting" on recoating, found that only heat-convertible oils and resins lift and the tendency reaches a maximum in a few days and then disappears. A lacquer thinner will dissolve the film before this maximum is reached but not after. A film which remains soluble may be recoated by spraying and will not lift.

<sup>27</sup> L. E. Barringer, U. S. P. 1,772,748, Aug. 12, 1930, to General Electric Co.; *Chem. Abs.*, 1930, 24, 5172. British P. 255,163, 1927, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1928, 680. French P. 649,284, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 2841.



the baking temperature, may be reduced by converting the A-stage alkyd resin to the C-stage in mass, before it is applied to the surface to be coated. The otherwise insoluble resin in this case is dispersed in a solvent by heating the resin in contact with the solvent in a closed vessel. Glyptal resin, for example, may be dispersed in acetone by heating at 150-170°C. in an autoclave for 36 hours.

A Glyptal baking lacquer (839-P) may be used with or without pigments on glass, glazed or unglazed porcelain, aluminum, copper, brass and a great many other metals.<sup>37</sup> It may be applied by brushing, dipping or spraying, to yield a flexible, insoluble, adherent and color-permanent coating. For spraying it should be thinned about 50 per cent with equal parts of alcohol and benzene. The pigments which may be employed are given in Table 47; when no pigment is used, a dark-yellow coating is obtained. Temperature and time are given in Table 48.

TABLE 47.—*Pigments for Use in Glyptal Enamels.*

Green:	Chrome green, prussian blue, chrome yellow
Red:	Vermilion, chrome red
Blue:	Prussian blue, ultramarine
Yellow:	Cadmium yellow, chrome yellow, yellow ochre
White:	Lithopone, timonox, titanox, pure titania, blanc white
Black:	Gilsonite, coal-tar or wood-tar pitch, carbon black

TABLE 48.—*Temperature and Time for Baking Glyptal (839-P) Films.*

Temperature in °F.	Time in Hours
260	10
300	4 5
350 ..	2
400...	1
450.....	25/60

According to Van Heuckeroth's<sup>38</sup> exposure tests, alkyd resins are superior to an oleoresinous product as metal primers under lacquers.<sup>39</sup> In finishing processes, it has been found that a lacquer has a rough surface due to uneven flowing, uneven surface shrinkage and due also to accumulation of spray dust and dust from the air. Smoothing of the coat can be accomplished by sanding and mist spraying. The latter procedure can be avoided by coating the articles with an alkyd resin, rubbing down with an abrasive material and then heating to 70-120°C. to eliminate the abrasion marks and to produce a smooth lustrous finish.<sup>40</sup> A method of treating aluminum vessels, developed by Brossman,<sup>41</sup> consists in scouring the vessel, filling it with an alkyd resin, heating to 90-110°C. for from 10-24 hours under a pressure of 90 lbs. per square inch, draining and baking at the same temperature for 10-12 hours to harden the resin in the pores. In finishes for zinc and aluminum die-cast parts, particular care in cleaning is necessary due to the variable porous nature of the castings. Baked-on alkyd enamels are preferred for finishing operations.<sup>42</sup> Another coating material for metal surfaces consists of a mixture of a synthetic resin which is capable of being hardened (phenol-

<sup>37</sup> General Electric Co., *Special Products Section Circ.* GEA, 1927, (Sept.), 840.

<sup>38</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1931, 399, 377; *Chem. Abs.*, 1932, 26, 608.

<sup>39</sup> The use of clear top varnishes on lithographed metal advertising signs in order to obviate the chalking and fading of certain colors is recommended by H. A. Gardner (*Amer. Paint, Varnish Mfrs. Assoc.*, 1933, 427, 230; *Brit. Chem. Abs.* B, 1933, 1068). Promising tests were shown by nitrocellulose and Rezoglas (polystyrene) plasticized with 25 and 50 per cent, respectively, of diphenyl phthalate, nitrocellulose lacquers with a high resin content of Rezyl No. 19 and Rezyl Balsam No. 33, and a "44-gal." modified phenol-formaldehyde-tung oil varnish. A baking oil primer is needed.

<sup>40</sup> F. M. Crytler, U. S. P. 1,904,417, April 18, 1933, to Jones-Dabney Co.; *Brit. Chem. Abs.* B, 1933, 1032.

<sup>41</sup> J. R. Brossman, British P. 375,012, 1931, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B, 1933, 969.

<sup>42</sup> H. Chase, *Synthetic and Applied Finishes*, 1934, 5, 208; *Brit. Chem. Abs.* B, 1935, 32.

formaldehyde or alkyd resin) with silicon or an acid-proof metal silicide. This is applied to metal tanks, enamelled apparatus and ceramic ware as a coating or lining, and subsequently hardened. Alternatively the resin may be applied and the silicon then incorporated before the hardening process.<sup>48</sup> A gold leaf decalcomania type of decoration can be applied to a surface of lacquered steel by means of an adhesive which includes an alkyd resin, with an overlying coating consisting of an oil-modified resin of the same general type.<sup>49</sup>

Another application of the alkyd resins is in the coating of tin cans to prevent the discoloration of crab meat. Due to the sulphide content of crab meat, it is necessary to keep metals from immediate contact. A lacquer consisting of 20 per cent of an alkyd resin, 40 per cent combined linseed and tung oil and 40 per cent petroleum thinner containing drier is sprayed on to the tin plates and baked at 250-375°F. The resulting coat is a non-conductor of electricity, impervious to moisture and contains no ingredients which will form sulphides.<sup>49</sup>

#### USE OF ALKYD RESINS IN PRINTING

Alkyd resins have found a number of applications in connection with the manufacture of inks for plain or relief printing.<sup>48</sup> Thus Fleischmann and Jordan<sup>48</sup> have prepared intaglio printing colors from a finely dispersed coloring material and a solution in a volatile organic solvent of an alkyd resin. The following examples illustrate the compositions used:<sup>48</sup> (1) The condensation product of glycerol, linseed oil, phthalic anhydride and rosin is dissolved in toluene, with Lithol Fast Scarlet R ground in; a drier being added if necessary. (2) Chrome yellow is added to a solution in benzyl acetate of the condensation product of ethylene glycol monolinoleic ester, glycerol and phthalic anhydride, with which lead-manganese resinate is subsequently incorporated. (3) Nitrocellulose, a rosin-modified glycerol phthalate and dibutyl phthalate are dissolved in ethylene glycol monoacetate and cyclohexanol and the resulting solution is ground with zinc green.

Scheiber<sup>49</sup> has employed for the preparation of printing ink a vehicle containing the ester of a polyhydric alcohol with 9,11-octadecadiene-1-carboxylic acid which is prepared by the vacuum distillation of castor oil acids. The esters may be boiled to an appropriate consistency before use. Davis,<sup>50</sup> in forming a type-impressible stencil sheet, used a glycerol phthalate resin made up from 200 parts of phthalic anhydride and 100 parts of glycerol. The reactants were heated for an hour at 185°C., whereupon the temperature was raised slowly to 210°C. and kept at this point until a sample on cooling gave a clear, brittle, yellow-colored resin without appreciable tack and with no stickiness. To 225 cc. of a 10 per cent solution of this resin in acetone were added 45 cc. of castor oil, 30 g. of chlorinated naphthalene, 15 g. of Japan wax and 15 cc. of paraldehyde. A small amount of nitrocellulose may also be added and the material is then coated onto a support such as yoshino paper and dried. The mixture forms a homogeneous semi-fluid mass at ordinary temperature.

<sup>48</sup> British P. 376,047, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 902.

<sup>49</sup> G. R. Enslinger, U. S. P. 1,872,131, Aug. 16, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 0062. British P. 405,696, 1922; *Brit. Chem. Abs. B*, 1934, 324. Canadian P. 327,322, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 1218.

<sup>50</sup> F. J. Donovan, U. S. P. 1,916,040, June 27, 1933, to Nathan Hirsch; *Chem. Abs.*, 1933, 27, 4601.

<sup>48</sup> E. Knebel, A. Hügel and H. Steinmeyer, German P. 591,456, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2463. W. Litskendorf, German P. 535,167, 1933; *Chem. Abs.*, 1934, 28, 1556.

<sup>49</sup> H. Fleischmann and O. Jordan, U. S. P. 1,737,339, Dec. 30, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 27, 533. British P. 307,577, 1929; *Brit. Chem. Abs. B*, 1930, 26. French P. 671,032.

<sup>48</sup> British P. 337,199, 1933, addn. to 307,577, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2011. French P. 700,593, 1930 and 696,699, 1930; *Chem. Abs.*, 1931, 25, 3385, 3184.

<sup>49</sup> J. Scheiber, German P. 523,377 and 532,456, 1933; *Chem. Abs.*, 1931, 25, 3184. See Chapter 43.

<sup>50</sup> A. B. Davis, U. S. P. 1,649,896, Nov. 15, 1927, to A. B. Dick; *Chem. Abs.*, 1928, 22, 466.

## MANUFACTURE OF LAMINATED GLASS

The condensation products from glycerol or glycol and phthalic acid have found application in the manufacture of laminated glass. The good adhesive properties of the alkyd resins, coupled with the fact that they do not darken appreciably on prolonged exposure to light, render them useful in this connection. Zola<sup>51</sup> employed as a basic resin for this purpose the product of condensation of glycerol with adipic or sebacic acid. Such a resin alone has a tendency to show sheeting lines in the laminated product, and to avoid this difficulty other resins are added, among which are other alkyd resins, phenol-formaldehyde resins, toluenesulphonamide derivatives and ester gum. The basic resin is ordinarily compounded with 60 per cent of toluene. The basic with the added resin is then dissolved in a solvent consisting of 45 per cent of heavy naphtha, 45 per cent of toluene and 10 per cent of ethyl acetate. In compositing the sheets of glass and cellulose ester plastic, the resin solution is sprayed in a thin film, which is allowed to dry in the atmosphere. The sheets are then placed together and the sandwich is exposed to heat and pressure. In a later development Zola<sup>52</sup> has used fatty acids or oils (castor, linseed, maize, tung and soya bean oil) as modifiers for the glycerol-phthalic anhydride resin.

Field and Haslett<sup>53</sup> have also employed alkyd resins either alone or mixed with other synthetic resins (phenol-formaldehyde or phenol-urea-formaldehyde) for manufacturing non-splintering glass. The mixed resins may be applied alone or with other materials such as Canada balsam, euphorbium resin or cellulose ester solutions. Sprenger<sup>54</sup> made a similar application of condensation products of the glycerol-phthalic anhydride type.

Laminations of glass, wood, textile materials or cellulose acetate sheets may be assembled in a bath containing an alkyd resin in the A-stage of condensation.<sup>55</sup> The resin is used in a solvent consisting of ethyl and butyl lactates and dichloroethylene. After removal from the bath the composite material is consolidated by compression at 300 lb. per square inch at 90-130°C.

Another method of manufacture of non-splintering glass is to utilize for cementing purposes one or more polybasic acid-polyhydric alcohol condensation products in a warm liquid or viscous condition. Cellulose derivatives or polyvinyl esters may also be incorporated.<sup>56</sup> The resin may also be applied in solution to the glass, dried and polymerized and the glass sheets then pressed on to the sheet of cellulose material.<sup>57</sup>

## APPLICATIONS OF ALKYD RESINS IN COATING COMPOSITIONS

Kienle and Adams<sup>58</sup> treat a solution of resin prepared from glycerol and phthalic anhydride containing excess acid, with an alkali to neutrality. The clear solution, decanted from the insoluble salts, can be mixed with basic

<sup>51</sup> J. C. Zola, U. S. P. 1,900,536, March 7, 1933, to Duplate Corp.; *Brit. Chem. Abs. B*, 1934, 96.

<sup>52</sup> J. C. Zola, U. S. P. 1,920,619, Aug. 1, 1933, to Duplate Corp.; *Chem. Abs.*, 1933, 27, 4896.

<sup>53</sup> C. H. Field and D. Haslett, *British P.* 321,178, 1928; *Brit. Chem. Abs. B*, 1930, 13.

<sup>54</sup> R. Sprenger, *German P.* 557,165, 1929, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1933, 27, 390.

<sup>55</sup> W. C. Dougan, *British P.* 355,604, 1930, to Newtex Safety Glass Co., Ltd.; *Chem. Abs.*, 1933, 27, 580.

<sup>56</sup> *British P.* 373,579, 1931, addn. to 363,933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 726,262. *French P.* 715,684, 1931; *Chem. Abs.*, 1932, 26, 2029. See Chapter 45.

<sup>57</sup> *French P.* 673,668, 1928, to Soc. anon. Saint-Gobain, Chauny et Cirey; *Chem. Abs.*, 1930, 24, 2568. See also Chapter 46.

<sup>58</sup> R. H. Kienle and L. V. Adams, U. S. P. 1,733,364, Dec. 2, 1930, to General Electric Co.; *Chem. Abs.*, 1931, 25, 424. *British P.* 234,248, 1927, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1928, 22, 4848. *German P.* 565,787, 1929, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1933, 27, 3501. *Canadian P.* 280,987, 1928, to Canadian General Elec. Co.; *Chem. Abs.*, 1928, 22, 3056. See Chapter 46.

pigments to form enamels. Litharge may be used as an ingredient in the preparation of a composition which consists of a drying oil acid-modified glycerol phthalate. The components are heated at 170-225°C. for 2.5-6 hours during which time 1-10 per cent of litharge, based on the weight of resin, is slowly added with agitation. The resin is cut in a solvent to remove excess litharge and any insoluble lead compounds. This treatment is found to impart improved water-resistance, increased rate of set-up and increased hardness.<sup>60</sup> The coatings formed are free from after-tack.<sup>60</sup> Alkyd resins incorporated with an inorganic softening agent (graphite, asbestos powder or talc) and a filler (red lead or litharge) are said to yield a resistant, acid-proof coating.<sup>61</sup> In this instance, for coatings consisting of multiple layers the hardening agent may be added to the final layer, the softeners being confined to the lower layers.

Barringer<sup>62</sup> has described an alkyd resin coating applied to an asbestos composition backing. A sheet composed of asbestos and portland cement is used as the foundation, this being given one or more coats of a solution of glycerol phthalate resin followed by baking the article for ten or twelve hours at 150-200°C. to convert the resin to a hard insoluble form. An alternative method of applying the coating is by sifting the powdered resin upon the surface while the article is at a temperature of about 200°C. The first coat is usually clear and acts as a primer. Indene, dibutyl phthalate or tricresyl phosphate can be used as plasticizers. These coatings have good heat-resistance and are very adherent, durable, odorless, impervious to liquids and are useful for refrigerator linings. Another method of applying these resinous substances to surfaces such as wood, metal, paper, porcelain or asbestos is to pass a stream of the finely powdered resin through a flame or other heating zone on to the surface, and then to bake the coated article.<sup>63</sup>

Wright<sup>64</sup> has described a composition for coating by spraying or dipping, formed from an alkyd resin in the B-stage with a pigment suspended in a volatile liquid (carbon tetrachloride, turpentine or paraffin hydrocarbons) in which liquid the resin does not tend to soften. The coated articles are baked from 2-12 hours at 125-180°C. The alkyd resin alone may also be dissolved directly in a mixture of solvents of graded boiling points (acetone, denatured alcohol, benzene and ethyl lactate) and the coatings formed from such a solution are first baked at 100° and subsequently at 200°C.<sup>65</sup>

Jaeger<sup>66</sup> has used the glycerol phthalate resins as an outer coating on candles to prevent drip while burning and to insure greater freedom from breakage. The coating may be applied by dipping or brushing and consists of alkyds or alkyds

<sup>60</sup> R. T. Ubben (U. S. P. 1,998,744, Apr. 23, 1935, to E. I. du Pont de Nemours & Co.) reported that water-resistant films are obtained if a polyhydric alcohol (approximately equivalent to that required to neutralize the excess acid) is added to an aqueous solution of alkyd resin containing a volatile base (ammonia or methylvamine), and baking the films resulting from such a composition.

<sup>61</sup> G. D. Patterson and R. A. Shive, U. S. P. 1,984,153, Dec. 11, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 854. Canadian P. 315,487, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 1812. E. I. du Pont de Nemours & Co., British P. 374,876, 1931, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1932, 808. See Chapter 44.

<sup>62</sup> British P. 360,944, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 235.

<sup>63</sup> L. E. Barringer, U. S. P. 1,721,367, July 16, 1929, to General Elec. Co. Canadian P. 280,936, 1928, to Canadian General Elec. Co. French P. 646,424, 1927, to Compagnie française Thomson-Houston.

<sup>64</sup> R. H. Kienle and L. V. Adams, British P. 354,544, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1932, 26, 3948.

<sup>65</sup> J. G. E. Wright, British P. 349,399, 1929, to British Thomson-Houston Co.; *Chem. Abs.*, 1932, 26, 2071. French P. 695,951, 1931, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1931, 25, 2896. German P. 582,170, 1933, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1933, 27, 5203.

<sup>66</sup> H. W. H. Warren and R. Newbound, British P. 306,914, 1927, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 23, 5333. French P. 662,156, 1928, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1930, 24, 515.

<sup>67</sup> A. O. Jaeger, U. S. P. 1,959,164, May 15, 1934, to the Selden Co.; *Chem. Abs.*, 1934, 28, 4620.

modified with phthalide,<sup>67</sup> phenol-aldehyde, phenol-furfural, nitrocellulose or natural resins.

A glycerol phthalate type resin has been utilized in the making of an artificial silk. The heated resin is extended into air at a temperature of 150-200°C. Also an acetone solution of alkyd resin may be passed into a coagulating bath and the filaments subsequently baked.<sup>68</sup>

Cellophane or a similar smooth-surfaced base can be coated with a solution of an alkyd resin and a plasticizing agent; the resulting coating is found to adhere firmly, while the surface is glossy and resistant to moisture and heat. On a viscose base, the resulting sheet has fair dielectric strength.<sup>69</sup>

### COATINGS ON RUBBER

Uncured rubber cloth or other products may be coated with a lacquer containing an alkyd resin made in the presence of a hydroxylated fatty oil and a urea-formaldehyde condensation product. The coating is hardened and the rubber is simultaneously vulcanized by treatment with a solution of sulphur chloride in carbon disulphide or naphtha.<sup>70</sup> It has been found that the limpness of latex-treated fabrics is obviated by previously mixing the aqueous rubber dispersion with an aqueous solution of an alkyd resin.<sup>71</sup> It is probably significant in this connection that a suspension of an alkyd resin in a mineral oil is stabilized by a few drops of a rubber solution.<sup>72</sup> In preparing artificial leather, a coat of rubber is applied to fabric, embossed and then coated with pigmented varnish containing oil and asphalt and finally baked to vulcanize the rubber and dry the varnish; the material may be subsequently "souped" with a composition consisting of pyroxylin and a pigmented alkyd resin.<sup>73</sup> Moreover the rubber may be coated directly with a castor oil-modified alkyd resin.<sup>74</sup> A lacquer formed from an alkyd resin, with drying oils or their acids to increase the elasticity, has been employed as a coating for wire before the application of a vulcanized rubber layer.<sup>75</sup> Heat-vulcanized rubber has been coated with a glycerol phthalate resin diluted with glycerol and glycol together with gelatin.<sup>76</sup>

Rubber can be attached to a rigid surface such as metal, porcelain, glass or wood by interposing the rubber with a glycerol phthalate resin and finally hardening with heat.<sup>77</sup> Certain alkyd resins will also plasticize chlorinated rubber.<sup>78</sup>

<sup>67</sup> See A. O. Jaeger, U. S. P. 1,941,474, Jan. 2, 1934, to the Selden Co.; *Chem. Abs.*, 1934, 28, 1880. See Chapter 45.

<sup>68</sup> H. Schuhmann and F. Streuber, German P. 553,005, 1928, to Allgem. Elektrizitäts-Ges.; *Chem. Abs.*, 1932, 26, 4718. Allgem. Elektrizitäts-Ges., British P. 303,867, 1929, to Internat. Gen. Electric Co., Inc.; *Brit. Chem. Abs. B*, 1930, 456. See, however, the work of W. H. Carothers and J. W. Hill, Chapter 41.

<sup>69</sup> H. L. Bender, British P. 355,318, 1930, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 25, 1006. For the use of alkyd resins to improve and preserve the "gut" of tennis rackets, see E. J. Barralet, British P. 338,223, 1929; *Chem. Abs.*, 1931, 25, 2255.

<sup>70</sup> E. A. Bevan and W. J. S. Naunton, British P. 351,581, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 447. French P. 720,868, 1931; *Chem. Abs.*, 1932, 26, 4207. German P. 572,221, 1931; *Chem. Abs.*, 1933, 27, 3113.

<sup>71</sup> W. E. Sanderson and F. J. Siddle, British P. 381,225, 1931, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1932, 1076.

<sup>72</sup> R. H. Kienle, British P. 385,970, 1932, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 4431. French P. 715,833, 1931, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 1994.

<sup>73</sup> A. N. Parrett, U. S. P. 1,818,575 and 1,818,576, Aug. 11, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 5580. French P. 721,014, 1931; *Chem. Abs.*, 1932, 26, 4204. See British P. 398,225, 1932; *Brit. Chem. Abs. B*, 1933, 1016.

<sup>74</sup> R. Hill and E. E. Walker, British P. 330,949, 1928; *Chem. Abs.*, 1930, 24, 6041.

<sup>75</sup> Allgemeine Elektrizitäts-Ges., British P. 303,868, 1928, to International General Electric Co.; *Chem. Abs.*, 1929, 23, 4515. See also British P. 379,913, 1932, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1933, 27, 3543.

<sup>76</sup> A. E. T. Neale, E. W. B. Owen, J. A. Wilson and D. F. Twiss, British P. 416,679, 1933, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs. B*, 1934, 1023. For the coating of paper, wood and the like with gelatin-glycerol phthalate, see C. M. Boyce, U. S. P. 1,978,406, Oct. 30, 1934, to J. R. Ditmars; *Chem. Abs.*, 1935, 29, 367.

<sup>77</sup> O. A. Thompson, British P. 388,776, 1933, to the B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 5909.

<sup>78</sup> W. Krumbhaar, *Official Digest Federation Paint Varnish Prod. Clubs*, 1934, 113, 33; *Chem. Abs.*, 1934, 28, 2939. See Chapter 55.

## USES OF ALKYD RESIN COATINGS WITH CELLULOSE ESTERS

The use of alkyd resins in conjunction with nitrocellulose or cellulose acetate in lacquers is one of the most important developments in this field in recent years.<sup>79</sup> Bradley<sup>80</sup> has shown that the Rezyls act as preservatives for nitrocellulose. Resins as a rule decrease the durability of the nitrocellulose film, but with the Rezyls the converse is true. As much as 4-5 parts of Rezyl may be mixed with 1 part of nitrocellulose, the durability of the resulting film being greater, within certain limits, the larger the amount of the added synthetic resin. With respect to mechanical properties, tensile strength, distensibility and durability, the alkyd resin functions primarily as a resin, nevertheless it acts to some degree as a plasticizer. The optimum percentage of alkyds for best results with nitrocellulose is probably very high.<sup>81</sup>

The compatibility of the Rezyls with nitrocellulose in a wide range of solvents has been examined by Hofmann.<sup>82</sup> Resins and solvents can be divided into two groups, the alcohol-soluble type and the hydrocarbon-soluble type. The alcohol-type resins are most easily soluble in the alcohol-type solvents and the hydrocarbon-type resin in the hydrocarbon-type solvents. In some "alcoholic" solvents (mesityl oxide, ethyl lactate or butyl Cellosolve) clear solutions and films were obtained, whereas in a number of solvents (sec-butyl acetate or amyl acetate) the addition of alcohol or toluene was needed to ensure satisfactory results. In general, compatibility is most readily obtained by using solvents and resins of corresponding types, that is, an alcohol-type solvent and an alcohol-soluble resin.

A cracked petroleum distillate (b.p. 130-150°C.), consisting essentially of monolefins, when added to monochlorobenzene was found by Lougovoy<sup>83</sup> to be a good diluent for nitrocellulose lacquers. Natural resins (rosin ester) and castor oil-modified glycerol phthalate resin as well as glycerol phthalate benzoate can be used along with nitrocellulose. Sec-butyl alcohol diluted with toluene produces a marked lowering of viscosity of the nitrocellulose coating composition without affecting toughness and durability. Isopropyl alcohol likewise has this property.<sup>84</sup> Diacetone alcohol, when mixed with unsaturated petroleum hydrocarbons of limited boiling range, acts as a nitrocellulose solvent. The addition of a higher alcohol is necessary to blend the diacetone alcohol and the hydrocarbons. Cottonseed oil fatty acid-modified glycerol phthalate can be added to this composition.<sup>85</sup>

Hofmann and Reid<sup>86</sup> determined that the resins from phthalic anhydride and ethylene glycol are compatible with cellulose acetate. They function in the combined role of resin and plasticizer. A lacquer containing 9 parts cellulose acetate, 7 parts glycol phthalate and 50 parts pigment when sprayed onto panels coated with an oleoresinous primer and surfacer gave films of good flexibility but of rather unsatisfactory adhesion. Using a pyroxylin primer and surfacer the results were

<sup>79</sup> Very few of the natural or synthetic resins are compatible with cellulose acetate. The "Santolites" (toluene sulphonamide) (see Chapter 34), some Rezyl balsams and some "Plasto" resins (see Chapter 11) give fairly satisfactory films with cellulose acetate, particularly when plasticized with ethyl phthalyl ethyl glycolate, methyl phthalyl ethyl glycolate and dibutyl phthalate. Cf. A. W. Heuckeroth, *Sci. Sect., Nat. Paint, Varnish, Lacquer Assoc., Inc.*, 1934, 458, 97; *Brit. Chem. Abs. B.*, 1934, 546.

<sup>80</sup> T. F. Bradley, *Paint Oil Chem. Rev.*, 1938, (15), 12, 17, (16), 10, 14.

<sup>81</sup> See H. Wolf and B. Rosen, *Farben-Ztg.*, 1933, 38, 989, 1020; *Chem. Abs.*, 1933, 27, 4425. A short review of the manufacture of alkyd resins for nitrocellulose plasticizers is given by J. McE. Sanderson, *Off. Digest, Fed. Paint, Varnish Prod. Clubs*, 1935, 143, 66; *Chem. Abs.*, 1935, 29, 2761.

<sup>82</sup> H. E. Hofmann, *Ind. Eng. Chem.*, 1931, 23, 127.

<sup>83</sup> B. N. Lougovoy, U. S. P. 1,913,679, June 13, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 4428.

<sup>84</sup> T. F. Bradley, U. S. P. 1,923,704, Aug. 22, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 5560. See U. S. P. 1,923,716, Aug. 22, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 5560. For the effect of various solvents on the viscosity of lacquers and alkyd resin solutions see C. Bogin, *Paint, Oil, Chem. Rev.*, 1935, 97 (9), 45; *Brit. Chem. Abs. B.*, 1935, 598.

<sup>85</sup> Carleton Ellis, U. S. P. 1,984,061, Dec. 11, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1935, 29, 948.

<sup>86</sup> H. E. Hofmann and E. W. Reid, *Ind. Eng. Chem.*, 1929, 21, 955.

more satisfactory. The strong influence of constituents on the properties of the film has been emphasized by Herzog, Hildesheimer and Medicus,<sup>87</sup> these investigators having examined the influence of a variety of organic compounds on nitrocellulose lacquers.

Lamb and Gilman<sup>88</sup> have explored the possibilities of using Rezyls with cellulose for leather dressings. Up to 3 parts of the resins for 1 part of nitrocellulose were used together with a solvent mixture consisting of ethyl acetate and ethyl lactate with a small quantity of butyl alcohol and up to 70 per cent of toluene as a diluent. The results were not satisfactory for glove leather, as an insufficient elasticity resulted. The following formula gave good results for Morocco leather: 40 parts of ethyl acetate, 80 parts of ethyl lactate, 40 parts of butanol, 240 parts of toluene, 16 parts of nitrocellulose (film), 48 parts of resin and 16 parts of ultramarine blue. A disadvantage common to most finishes with a cellulose ester base is that, if sufficient pigment is added to give a good covering, the finish loses all its brilliance and tends to become brittle. Apart from this disadvantage, the glycerol phthalate resin imparts softness, flexibility and resistance to deterioration by ultraviolet light. Nitrocellulose varnishes which remain elastic and which are resistant to changing temperature conditions and useful for covering natural and artificial leather are prepared by introducing zinc naphthenates into nitrocellulose, together with alkyd resins.<sup>89</sup>

#### ALKYD RESINS IN LACQUER COATINGS AND AS PRIMER COATINGS

Work carried out in the author's laboratory has resulted in a number of direct applications of glycerol-phthalic anhydride resins with cellulose esters. Thus a primer coating of an alkyd resin on wood or metal was found to be satisfactory with a superimposed coating of a nitrocellulose composition.<sup>90</sup> Wood lacquers for furniture coating should possess great hardness and toughness and enough elasticity to withstand contraction and expansion. A low-viscosity nitrocellulose is used which may be prepared by boiling motion-picture film in water rendered slightly alkaline and heating the emulsion-free material to 160°C. for 2-5 seconds. A castor oil-phthalic-glyceride is prepared by heating 47 parts of glycerol, 80 parts of phthalic anhydride and 40 parts of castor oil under reflux. To make up a gloss-white enamel, 12 parts of low viscosity nitrocellulose, 6 parts of castor oil-phthalic-glyceride, 5 parts of zinc oxide, 5 parts of titanox, 5 parts of dibutyl phthalate, 10 parts of butyl propionate, 10 parts of butyl acetate, 5 parts of butyl alcohol, 10 parts of ethyl acetate and 30 parts of toluene are used.<sup>91</sup> Weber<sup>92</sup> prepared a cellulose ester composition for films and molded articles by incorporating with cellulose nitrate the reaction product of a vegetable oil (corn, tung or blown rapeseed oil) and an organic acid obtained from either castor or soya bean oil together with a polyhydric alcohol and phthalic anhydride. Nitrocellulose, when admixed with a rosin-glycerol phthalate resin which is soluble in nitrocellulose solvents, gives rise to a coating composition.<sup>93</sup>

Precipitation of the nitrocellulose during evaporation of volatile solvents (acetone, ethyl acetate) and consequent "blushing" of the film can be prevented

<sup>87</sup> R. O. Herzog, A. Hildesheimer and F. Medicus, *Z. angew. Chem.*, 1921, 57; *Kunststoffe*, 1921, 11, 46.

<sup>88</sup> M. C. Lamb and J. A. Gilman, *Cuir tech.*, 1932, 21, 138; *Chem. Abs.*, 1932, 26, 3404.

<sup>89</sup> K. I. Meltsner, *Ovладение Tekhniki Koshobuynoe Proizvodstvo*, 1932, (8), 27; *Chem. Abs.*, 1934, 28, 7559.

<sup>90</sup> Carleton Ellis, U. S. P. 1,745,893, Feb. 4, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1930, 24, 1753.

<sup>91</sup> Carleton Ellis, U. S. P. 1,927,036, Sept. 19, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 5931. *British P.* 388,567, 1933; *Chem. Abs.*, 1933, 27, 4699.

<sup>92</sup> H. M. Weber, U. S. P. 1,690,318, Nov. 6, 1928, to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 512.

<sup>93</sup> H. M. Weber, U. S. P. 1,723,776, July 30, 1929, to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 4532. *Canadian P.* 311,690, 1931.

by incorporating glycerol-fatty acid resins<sup>94</sup> or by means of balsams of analogous types. Such a balsam can be prepared from 106 parts of diethylene glycol, 100 parts of coconut oil and 148 parts of phthalic anhydride.<sup>95</sup>

A sulpho-chlorinated fatty acid-modified glycerol phthalate resin produced from phthalic anhydride, glycerol, cottonseed fatty acids and sulphur monochloride is adaptable for use with nitrocellulose in coating compositions.<sup>96</sup> A quick-drying coating material is obtained by mixing nitrocellulose of medium viscosity (e.g., "4-10 sec.") with an alkyd resin which is soluble in benzene anhydrous methyl alcohol mixtures.<sup>97</sup> A glycerol benzoate-salicylate-abietate resin may be rendered light in color by cooling the reaction product under reduced pressure or in an inert gas such as nitrogen.<sup>98</sup>

The incorporation of castor oil with the glycerol-phthalic anhydride resin for admixture with nitrocellulose affords a further method of modifying the resulting coating material.<sup>99</sup> The use of castor oil renders the product soluble in ethyl and butyl acetates or mixtures of these with the corresponding alcohols. A resin prepared from 74 parts of phthalic anhydride, 45 parts of glycerol and 33 parts of castor oil at 290°C. is hard; the incorporation of a larger proportion of castor oil yields a softer product. Increased quantities of the softer type of composition, admixed with nitrocellulose, renders possible the production of more flexible and longer-wearing artificial leathers. Added to this, the elimination of castor oil odors and that of rancidifying oils is of special value in the manufacture of artificial leather.

#### COATINGS ON PAPER

Alkyd resins in conjunction with nitrocellulose have been applied to the production of a grease-resistant paper. A development by Bradley<sup>100</sup> utilizes a composition such as the following: 40 parts (by weight) of low-viscosity nitrocellulose, 40 parts of cottonseed-phthalic glyceride resin, 20 parts of dibutyl phthalate, 135 parts of ethyl acetate, 135 parts of benzene and 5 parts of paraffin wax. The paper is ordinarily run over rolls or through a bath of the material. The wax in the solution substantially checks the evaporation of the solvents at room temperature; this is important in that it largely eliminates the possible toxic hazard of benzene vapors. The paper is dried at 140°F. In order to secure proper impregnation of the paper it is best to submit the coated material to the action of hot calender rolls. A coating of greatly reduced inflammability is secured by a high resin content, by the use of tricresyl phosphate as a plasticizer and by the employment of hydrated inorganic bodies as fillers.

A further application of modified alkyd resins is in the production of grease-resisting box board and grease-proof paper. Paper or board, which has been made from ground wood and sulphite pulp, or similar fibrous material, is used and is impregnated with wax which has been added in the form of an emulsion in the beater. A typical composition is the following: 20 parts of nitrocellulose solution, containing 20 per cent of low viscosity nitrocellulose in acetone, are mixed with 8 parts of a resin solution (cottonseed-phthalic-glyceride resin dissolved in an equal volume of acetone). One part of dibutyl phthalate is added. The solution, which is of low viscosity, may

<sup>94</sup> Carleton Ellis, U. S. P. 1,923,714, Aug. 22, 1933, to Ellis-Foster Co.; *Brit. Chem. Abs.* B, 1934, 546.

<sup>95</sup> T. F. Bradley, U. S. P. 1,923,715, Aug. 22, 1933, to Ellis-Foster Co.; *Brit. Chem. Abs.* B, 1934, 546.

<sup>96</sup> Carleton Ellis, U. S. P. 1,811,115, June 28, 1931; *Chem. Abs.*, 1931, 25, 5049.

<sup>97</sup> Carleton Ellis, U. S. P. 1,824,757, Sept. 22, 1931, to Ellis-Foster Co.; *Chem. Abs.*, 1932, 26, 324.

<sup>98</sup> French P. 719,571, 1931; *Chem. Abs.*, 1932, 26, 3943.

<sup>99</sup> British P. 327,095 and 327,096, to Ellis-Foster Co.; *Brit. Chem. Abs.* B, 1930, 570. French P.

667,918 and 667,919, 1929; *Chem. Abs.*, 1930, 24, 1529. See Chapter 43.

<sup>100</sup> T. F. Bradley, U. S. P. 1,863,204, June 14, 1933; *Chem. Abs.*, 1933, 26, 4190.

<sup>101</sup> T. F. Bradley, U. S. P. 1,896,315, Feb. 7, 1933; *Chem. Abs.*, 1933, 27, 2579.



be applied to paper by brushing or coating. Paper of this type is used in making boxes, cartons, ice cream containers and the like.<sup>101</sup>

Paper with a high  $\alpha$ -cellulose content can be impregnated with an alkyd resin to form a translucent heat-resistant paper useful for shades of lamps. The paper is made from spruce chips digested with sulphurous acid, blown and washed. About 5 per cent of the  $\beta$ - and  $\gamma$ -cellulose are left in the paper to act as a binding agent.<sup>102</sup>

A stratified film for decorative purposes described by the author<sup>103</sup> has a stratum, such as a pigmented nitrocellulose mixture, with an overlying protective stratum of nitrocellulose and a compatible resin of the oil-glyceride type. The top layer is free from pigment and is transparent. A waterproof brilliant surface is obtained on paper, cloth or skins by coating with nitrocellulose, a plasticizing agent consisting of a blown oil and finally covering with an alkyd resin varnish.<sup>104</sup>

#### OTHER CELLULOSE ESTER-ALKYD COATING COMPOSITIONS

A considerable number of resins of the glycerol-phthalic anhydride type, but varying in their exact constituents, have been suggested for use with nitrocellulose in coating and filling compositions. The alkyd resin may be derived from a polybasic acid (phthalic, halogenated phthalic acid or aliphatic dibasic acids<sup>105</sup>) and a polyhydroxy alcohol (glycerol, the hydroxyalkyl ethers of glycerol,<sup>106</sup> the hydroxyalkyl ethers of glycol,<sup>107</sup> pentaerythritol or sorbitol<sup>108</sup>). In place of nitrocellulose, the lower fatty acid esters of cellulose can be employed. Cellulose triacetate or butyrate or acetone-soluble cellulose acetate<sup>109</sup> can be incorporated with condensation products of phthalic<sup>110</sup> or aliphatic acids with ethylene, butylene glycol<sup>111</sup> or pentaglycerol.<sup>112</sup> In one example, nitrocellulose, a condensation product of succinic acid and glycerol, and tricresyl phosphate are dissolved in ethylene glycol monoethyl ether, ethyl alcohol and methyl acetate. Moreover ethyl cellulose can be blended with glycerol linoleate-ricinoleate-phthalate, or benzyl cellulose and mixed with glycerol abietate-palmitate-maleate.<sup>113</sup>

The adhesion of cellulose lacquers to smooth surfaces is improved by incorporation of about 5 per cent of alkyd resin previously plasticized with oleic acid. A primer containing an alkyd resin plasticized with materials such as oleic acid or tricresyl phosphate, and cured by heat treatment *in situ*, is also found to improve the flexibility of insulating varnishes.<sup>114</sup> One or two coats of the primer are applied and stoved for 1 minute at about 310°C., subsequent coatings of oil varnish being stoved for 1 minute at 350°C. Resins prepared from non-resinous organic acids have a notable resistance to water. Increase in the amount of

<sup>101</sup> Carleton Ellis, U. S. P. 1,892,939, Jan. 3, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 2301.

<sup>102</sup> F. O. Reiss, British P. 397,550, 1933, to Aladdin Industries, Ltd.; *Chem. Abs.*, 1934, 28, 1538.

<sup>103</sup> Carleton Ellis, U. S. P. 1,773,974, Aug. 26, 1930; *Chem. Abs.*, 1930, 24, 5172.

<sup>104</sup> E. I. du Pont de Nemours & Co., French P. 764,834, 1934, to Soc. française Duco; *Chem. Abs.*, 1934, 28, 6002. British P. 426,790, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.*, B, 1935, 562.

<sup>105</sup> British P. 322,466, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2600. French P. 669,278, 1929; *Chem. Abs.*, 1930, 24, 1753. British P. 330,909, addn. to 322,466; *Chem. Abs.*, 1930, 24, 6040.

<sup>106</sup> British P. 322,539, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2904. See British P. 330,910; *Chem. Abs.*, 1930, 24, 6040.

<sup>107</sup> British P. 322,538, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2904.

<sup>108</sup> British P. 322,537, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2904.

<sup>109</sup> British P. 322,540, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 157.

<sup>110</sup> British P. 322,541, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 157.

<sup>111</sup> British P. 322,542, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 157.

<sup>112</sup> British P. 322,543, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 157.

<sup>113</sup> British P. 330,895, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 958.

<sup>114</sup> H. W. H. Warren and A. T. Ward, British P. 303,915 and 303,936, 1927, to Brit. Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B, 1929, 255. French P. 35,869, 1928 and 38,115, 1930, addns. to 649,384, 1927, to Compagnie française-Thomson-Houston; *Chem. Abs.*, 1930, 24, 4175; 1931, 25, 5584; 1929, 23, 2841.

monobasic acid used results in a lowering of the softening or melting point of the composite resin and renders it more readily soluble.<sup>115</sup>

Free acids have been found to have a plasticizing action on nitrocellulose films. Besides the higher fatty acids, phthalic and benzoic acids exercise definite softening action in thin nitrocellulose films. The presence of an ordinary type of plasticizer (tricresyl phosphate, dibutyl phthalate) seems to be necessary to prevent the acid from crystallizing. When the ordinary plasticizer is omitted, the acid crystallizes during the evaporation of the solvent and this often leads to the formation of novel and artistic finishes. When this does happen, the plasticizing action of the acid is lost.<sup>116</sup>

Nebel<sup>117</sup> has described a sanding sealer consisting of a cellulose derivative, a sanding promoter (calcium or zinc stearate) and a resin formed from glycerol, phthalic anhydride, rosin and stearic acid. An oil-modified alkyd resin, together with a plasticizer if required, may be used for coating sheets of regenerated cellulose. The coating is dried subsequently, at a raised temperature, and is non-tacky, moisture-proof and flexible.<sup>118</sup> Kramer<sup>119</sup> utilized phenoxyethyl phthalate, methylphenoxyethyl phthalate or methylphenoxyethyl laurate as softeners for lacquer compositions containing cellulose acetate.

A mixture of cellulose acetate or similar ester of cellulose with a relatively large amount of plasticizer and of alkyl phthalate or tartrate, or of a glycerol ester, has been found to yield a good insulating material.<sup>119a</sup> A duplex waterproof foil containing an alkyd resin as one of its constituents is made by the following method. A layer containing nitrocellulose waterproofed by inclusion of a wax (Japan wax), a fat (lanolin) or paraffin wax, together with an oil-soluble alkyd resin is superimposed by casting on a cellulose acetate film.<sup>120</sup>

Cellulose esters can be colored before esterification. Cotton linters are first dyed by means of a vat dye, the dyed cellulose esterified with an organic acid (acetic or formic) and the product used with an admixture of glycerol phthalate resin modified with phthalide, in which some of the same dye has been dissolved.<sup>121</sup>

A non-blushing nitrocellulose lacquer, described by Rogers<sup>122</sup> contains a cumarone-indene resin<sup>123</sup> melting above 110°C. and an alkyd resin. The total resin is not more than 18 per cent by weight of the lacquer, while the cumarone-indene constituent makes up approximately 25 to 40 per cent of the total resin.

The proportion of alkyd resin which may be added to a cellulose varnish and form a clear solution is said to be increased by the addition of so-called homogenizing agents.<sup>124</sup> Compounds such as nitrobenzene, benzaldehyde and pyridine have this property. For example, a mixture of 1.5 kg. of a 21 per cent solution of nitrocellulose and 1.0 kg. of a 50 per cent solution of phthalic acid-glycerol resin is cloudy, but on addition of 1 kg. of nitrobenzene to the mixture the turbidity disappears and hard, clear films result when the solution is employed as a varnish.

<sup>115</sup> H. M. Weber, U. S. P. 1,897,015, Feb. 7, 1933, to Ellis-Foster Co.; *Brit. Chem. Abs.* B, 1933, 928.

<sup>116</sup> T. F. Bradley, U. S. P. 1,946,479, Feb. 13, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 2554.

<sup>117</sup> W. Nebel, U. S. P. 1,973,649, Sept. 11, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 7044. British P. 377,724, 1932; *Chem. Abs.*, 1933, 27, 4108. Canadian P. 327,818, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 1529.

<sup>118</sup> W. L. Hyden and J. C. Sieman, U. S. P. 1,973,669, Sept. 11, 1934, to Du Pont Cellophane Co., Inc.; *Chem. Abs.*, 1934, 28, 7018. W. H. Charch, British P. 330,483, 1931; *Brit. Chem. Abs.* B, 1932, 1041.

<sup>119</sup> R. H. Kramer, U. S. P. 1,874,310, Aug. 30, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 6164. British P. 314,571, 1928, to Nobel Industries, Ltd.; *Brit. Chem. Abs.* B, 1929, 728.

<sup>119a</sup> V. E. Yarsley, British P. 355,654, 1930, to Non-inflammable Film Co., Ltd.; *Brit. Chem. Abs.* B, 1931, 1016.

<sup>120</sup> G. A. Staley, British P. 356,146, 1930, to Non-inflammable Film Co., Ltd.; *Brit. Chem. Abs.* B, 1931, 1045.

<sup>121</sup> A. O. Jaeger, U. S. P. 1,902,774, June 12, 1934, to the Selden Co.; *Chem. Abs.*, 1934, 28, 4918.

<sup>122</sup> A. Rogers, U. S. P. 1,884,355, Oct. 25, 1932, to Barrett Co.

<sup>123</sup> See Chapter 6.

<sup>124</sup> Allgem. Elektrizitäts-Ges., British P. 312,923, 1930, to International General Electric Co., Inc.; *Chem. Abs.*, 1930, 24, 930. German P. 550,001, 1937, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1932, 26, 5221.

The quantity of the homogenizing agent needed depends on the solvent and also on the degree of condensation of the alkyd resin. The amount of nitrobenzene needed is found to be decreased by the addition of ethylene glycol. The efficacy of a substance such as nitrobenzene in rendering a varnish homogeneous falls off as the softening point of the alkyd resin is raised. The general value of the softening point should be about 125°C.

Clark<sup>126</sup> found that cellulose-ester films for photographic purposes were obtainable by incorporating compounds such as diphenyl orthophthalate with nitrocellulose. The general method of preparing such a film is illustrated by the following example: 300 to 600 parts of a mixture of acetone and methyl alcohol are incorporated with 100 parts of nitrocellulose, 5 to 100 parts of fusel oil, or normal butyl or isobutyl alcohol, and from 1 to 45 parts of diphenyl orthophthalate. This composition is found to give a flexible film. The use of cellulose ester varnish incorporating 0.25 to 5 per cent glycerol butyl phthalate has been recommended as a protective coating for cellulose nitrate lacquer against the action of light.<sup>126</sup>

Cellulose esters are miscible with glycerol esters of aromatic monobasic acids. Plinatus,<sup>127</sup> in finding a close analogy between the effect of camphor on cellulose esters and that of esters of organic acids, proposed the use of these esters as a substitute for camphor in the manufacture of celluloid. By varying the quantity of the acid ester (benzoic-glycerol esters),<sup>128</sup> products were obtained which were hard and horn-like, of medium hardness or finally, of rubber-like softness. The cellulose esters are mixed with the acid esters and the mixture is worked into a homogeneous mass between heated rollers in a kneading mill. During this process the cellulose esters form a homogeneous solution which afterwards gelatinizes or solidifies. These compounds have been utilized in the production of artificial leather,<sup>129</sup> the gelatinized mixture being applied to a flexible base.

<sup>126</sup> H. T. Clark, U. S. P. 1,398,939, Nov. 29, 1921, to Eastman Kodak Co.; *Chem. Abs.*, 1922, 26, 830.

<sup>126</sup> British P. 371,901, 1930, to Eastman Kodak Co.; *Brit. Chem. Abs.* B, 1932, 778. For the use of other alkyd resins see Internat. General Electric Co., Inc., British P. 315,355, 1929, to Allg. Elektricitäts-Ges.; *Brit. Chem. Abs.* B, 1930, 1092.

<sup>127</sup> W. Plinatus, British P. 16,940, 1913; *J.S.C.I.*, 1915, 34, 793. French P. 476,991, 1914; *J.S.C.I.*, 1916, 35, 597. See S. de V. Shipley and G. C. Given, U. S. P. 1,533,616, Apr. 14, 1925, to Atlas Powder Co.; *J.S.C.I.*, 1925, 44, 514B. British P. 236,190, 1924; *Chem. Abs.*, 1926, 20, 997. Cf. also Allgem. Elektricitäts-Ges., British P. 341,535, 1928, to International General Electric Co.; *Chem. Abs.*, 1933, 27, 544. W. H. Moss and B. B. White, British P. 312,133, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs.* B, 1930, 726.

<sup>128</sup> For the use of mono- and di-glycerol esters of benzoic and naphthoic acids in cellulose ester films, see French P. 461,544, 1913, to H. Dreyfus; *Chem. Abs.*, 1914, 8, 3589.

<sup>129</sup> W. Plinatus, Canadian P. 298,527, 1930, to Proc. et appareil a fabriquer du cuir artificiel.

## Chapter 48

### Drying Oil Alkyd Resins Uses As Coatings. Varnishes

The underlying aim of the development of synthetic resin finishes has been, not in the preparation of synthetic substitutes to match natural products, but rather in the production of tough flexible materials without the known shortcomings of the natural resins. The best type of synthetic resin varnish or paint vehicle has been produced by condensing the resin components and the oil acids directly, so that distinct chemical compounds of unique properties are obtained, rather than by the nondescript procedure of dissolving a prepared resin in the drying oil.<sup>1</sup> The chemical processes have the additional advantage of lending themselves to strict control, whereby a high grade of uniformity and reproducibility of material may be achieved.

Alkyd resins of the oxidizing type (see Chapter 44) are made by incorporation of drying oil acids in a glycerol-phthalic anhydride type of resin.<sup>2</sup> This class covers a variety of substances, from hard solids approximating in properties natural resins to viscous liquids resembling drying oils. They may be used alone as the binding medium or may be admixed with other resins, oils, varnishes, or nitrocellulose. Although the consistency, acid number, and certain other properties of the oxidizing resins may vary considerably, the quality of high resistance to weathering is common to all. One factor in attaining durability is the relatively high elasticity of these resins, which is greater than that of other known varnish films of equivalent oil length. This may be seen from the following comparison of the Kauri reduction values of an oxidizing Rezyl with two of the durable phenol-formaldehyde types of resin.<sup>2a</sup>

<i>Material tested</i>	<i>Kauri Reduction Value</i>
Phenol-formaldehyde resin, ester gum modification—12-gallon varnish . . . . .	Below 0
Phenol-formaldehyde resin, unmodified—12-gallon varnish . . . . .	10-20
Rezyl (corresponding to 12-gallon oil length) . . . . .	50-60

Owing to this inherent elasticity, the use of oxidizing oils can be minimized, thereby lessening that slow destructive oxidation which leads to loss of gloss and flexibility.

#### INDUSTRIAL APPLICATION OF OXIDIZING ALKYD RESINS

Oxidizing alkyd resins have found industrial application in a variety of forms, covering a range of hardness, flexibility, and drying characteristics which renders possible their use in almost the entire group of paint products. Certain of the

<sup>1</sup> D. G. Hopkins, *J.S.C.I.*, 1932, 51, 186. J. Scheiber, *Farbe u. Lack*, 1932, 55, 73; *Chem. Abs.*, 1932, 26, 2331. M. Jeanny, *Rev. gen. mat. plast.*, 1935, 11, 10, 44; *Chem. Abs.*, 1935, 29, 3179. K. Buser, *Farben-Ztg.*, 1934, 39, 1240, 1263; *Chem. Abs.*, 1935, 29, 1267. Carleton Ellis, *Ind. Eng. Chem.*, 1933, 25, 128. Cf. *J.S.C.I.*, 1931, 50, 513. See also H. Ulrich, *Farben-Ztg.*, 1934, 39, 1094; *Chem. Abs.*, 1935, 29, 2859.

<sup>2</sup> Some of the trade names for these types of resin are Rezyl, Glyptal, Dulux and Alkydal.

<sup>2a</sup> T. F. Bradley, *Off. Digest, Fed. Paint, Varnish Prod. Clubs*, 1931, 535.

Rezyls<sup>a</sup> are not miscible with drying oils or with the usual oleo-resinous varnishes, but may be employed in xylol solution. For example, a solution consisting of 60 per cent Rezyl and 40 per cent xylol may be thinned to brushing- or spraying-consistency with equal parts of xylol, dipentene and mineral spirits, or of xylol and turpentine containing 2 per cent of pine oil. The petroleum-tolerance of such Rezyls is low, generally being of the order of 30 per cent or less.

The oil-soluble Rezyls<sup>a</sup> may be dissolved in most types of drying oils in the raw state. However, when the oils are bodied, solubility of the resins decreases. Rezyls of this series have a high petroleum-tolerance also, and can be dissolved directly in petroleum thinners. Hydrogenated petroleum hydrocarbons are much better solvents and compare favorably with coal-tar hydrocarbons.<sup>b</sup> The resins may be treated as varnish gums, and cooked with drying oils to form varnish bases. Thus, Rezyl 110 may be cooked with an equal weight of tung oil for several hours at 190-205°C. Better body and gas-resistance may be obtained by heating to 280°C., but the operation must be carried out rapidly to avoid formation of an insoluble gel. Addition of linseed oil, rosin, ester gum or phenol resins enhances gas-proofness. The oil-treated Rezyls have great flexibility, but are too soft for some purposes.

Carbonate pigments (white lead, whiting and colors based on them) should be avoided, since reaction occurs, with evolution of gas, on storage. Basic pigments, e.g., zinc oxide or chrome orange, thicken to some extent with the harder Rezyls, which have an acid number 45-60, but may be used in any proportion with those Rezyls<sup>a</sup> which have very low acid numbers. Zinc oxide, however, tends to produce hard and brittle films. When alkyd resins are used as pigment vehicles in enamels, care must be exercised to avoid contamination with varnish and oil products, or undue exposure to the air, during the grinding process.

The commercially produced oil-soluble Rezyls are used as paint vehicles both in paints where the Rezyl is the sole film-forming binder, and also in conjunction with drying oils. Paints of the latter type have improved working qualities and a wide range of application. An example of a quick-drying Rezyl paint vehicle is:<sup>c</sup>

Rezyl 110. . . . .	105 lbs.
Xylol or turpentine. . . . .	45 lbs.
Mineral spirits . . . . .	100 lbs.
Lead linoleate . . . . .	2 lbs.
Cobalt linoleate. . . . .	$\frac{1}{4}$ lb.

Oxidizing Rezyls have found use also in the replacement of a part, or all, of the bodied linseed oil in printing inks. For this purpose the softer, mineral spirit-soluble resins are best. Quicker drying and a better gloss are obtained as well as better color-retention and resistance to grease and wax. Rezyls may be mixed also with overprint varnish for improved elasticity and adhesion.

The durability of oxidizing alkyd resins, when used in quick-drying house paints, compares very favorably with that of Amberol or ester gum spar varnishes.<sup>d</sup> Test panels, treated with a clear film of hard, medium or soft linseed fatty acid-glycerol phthalate resins, showed perfect condition after 10 months exposure, while similar panels treated with a 46 gal. F7 Amberol spar varnish, and with

<sup>a</sup> E.g., Rezyls 113, 114 and 1102 of the American Cyanamid Company.

<sup>b</sup> E.g., Rezyls 110, 1103 and 116 of the American Cyanamid Company.

<sup>c</sup> W. J. Sweeney and J. H. Tilton, *Ind. Eng. Chem.*, 1934, 26, 693.

<sup>d</sup> E.g., Rezyl 116, the acid number of which is 6.9.

<sup>e</sup> American Cyanamid Co.'s circular, "Rezyls and Teglacla."

<sup>f</sup> L. K. Scott, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1931, 404, 532; *Chem. Abs.*, 1933, 26, 1139. See also L. K. Scott, E. J. Probeck and O. Mileti, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 370, 437; *Am. Paint J.*, 1930, 14 (52A), 31; *Paint, Oil, Chem. Rev.*, 1930, 90 (17), 84.

a 53 gal. ester gum varnish, failed completely. In paints composed of a variety of pigment mixtures, those with a linseed fatty acid-glycerol phthalate vehicle proved superior to the corresponding standard linseed oil paints. An alkyd resin film (modified by tung oil) on food containers and posters proved to be durable and non-yellowing under tropical conditions.<sup>9</sup>

Windsor<sup>10</sup> has discussed the outstanding advantages of synthetic resin enamels over oil enamels and has reviewed the influence of various factors, viz., time of setting up before baking, minimum baking time, and baking temperature in obtaining the most desirable properties such as hardness, flexibility, alkali- and acid-resistance.<sup>11</sup>

#### FILM-FORMING PROPERTIES OF OXIDIZING RESINS

The film-forming properties of alkyd resins have been studied by Kienle and Ferguson.<sup>12</sup> These workers distinguish three classes of resin: non-convertible, heat-convertible, and oxygen-convertible. Solutions of heat-convertible resins are transformed to the hard, insoluble form by baking. Oxygen-convertible resins (e.g., oxidizing alkyds) require only exposure to the air, the action of heat being merely to assist the oxidation, as with oil-base varnishes. At any one temperature, the oxidizing resins are transformed much more rapidly than the heat-convertible resins. Esters, acetone, or alcohol-mineral naphtha mixtures are solvents for the drying alkyds, and the solutions permit of considerable dilution with aliphatic hydrocarbons. Films formed are very adherent and smooth, with a rapid initial hardening. They possess essentially the same properties as the films from heat-convertible alkyd resins, with an additional pronounced film-building characteristic.

In order to get the best film, it is important that oxidizing alkyd resins should not contain any large amount of free fatty acids. In contrast with drying oils and oxidizing alkyds, the free fatty acids of drying oils do not dry when exposed to the air. They oxidize readily but do not form tough films. The behavior of free unsaturated acids was studied by Eibner and Jung<sup>13</sup> who found that films of acids containing many double bonds oxidize faster than those with few, but are less stable towards water. When mixed with red lead or white lead to form a paint, the acids yield a film in 1-4 days, also when exposed to water they show increasing susceptibility with increase in the number of non-conjugated double bonds.  $\alpha$ -Linolenic acid was found to oxidize in 8-10 days to a film tougher than that from linoleic acid. It yellowed more in winter than in summer and browned at 100°C.  $\alpha$ -Eleostearic acid oxidized in 6-8 days and turned less yellow than the linolenic acid film. It yellowed strongly in the oven, and showed poor adhesion to glass. Clupanodonic acid, with 4 double bonds, oxidized rapidly, browning at room temperature and, as follows from the high unsaturation, was the least stable towards water of all the films examined.

Gelation of oils during bodying is accelerated by a supply of energy in the form of heat, light, or electrical activation.<sup>14</sup> The phenomenon of gelation may oc-

<sup>9</sup> H. Nolte, *Farbe u. Lack*, 1933, 559, 569, 593, 605; *Brit. Chem. Abs. B*, 1934, 210.

<sup>10</sup> E. W. Windsor, *Ind. Finishing*, 1933, 9 (2), 22; *Chem. Abs.*, 1933, 27, 615.

<sup>11</sup> A body enamel which gasoline and alcohol cannot damage, and which is highly resistant to the deteriorating effect of strong sunlight, has been developed by Ford Motor Co. engineers, and is being used on the 1934 models. It is said that this type of finish uses soya bean oil as an ingredient, and that a special technique of body preparation and finish application is necessary before the enamel can be used in mass production. *Synthetic & Applied Finishes (London)*, 1935, 6, 7. See also J. L. McCloud, *Iron Age*, 1934, 133 (Aug. 2), 24.

<sup>12</sup> R. H. Kienle and C. S. Ferguson, *Ind. Eng. Chem.*, 1929, 21, 849. See Chapter 41.

<sup>13</sup> A. Eibner and V. Jung, *Chem. Umschau. Fette, Öle, Wachse, Harze*, 1931, 38, 267, 281; *Chem. Abs.*, 1932, 26, 898.

<sup>14</sup> J. S. Long and W. S. W. McCarter, *Ind. Eng. Chem.*, 1931, 23, 798.

cur also at room temperature under the influence of high pressures, or in the presence of metallic chlorides. Oxidation is a contributory cause and metallic driers function as catalysts not only of the oxidation reaction, but also of polymerization directly. According to Kienle,<sup>15</sup> the actual mechanism of gelation of synthetic resins is still uncertain. The chemical view of polymerization, whereby molecules are linked by primary valence-forces, applies successfully to many types of resin.<sup>15a</sup> Where straight-chain unions occur, non-convertible polymers are formed; where intertwining branched chains can result, the polymers are convertible. In general there will be obtained a mixture of polymers, in which small molecules of low degrees of condensation are associated with highly polymerized macromolecules. This leads to the formation of a colloidal system, and permits depolymerization, or reformation of a sol system, on appropriate treatment with a solvent. Thus, sols may be prepared from cured alkyd resins, or heat-converted drying oils, by simple prolonged treatment with a solvent in an autoclave. Clear transparent sols of cured glycerol phthalate in glycol diacetate, and of linseed oil gel in benzyl benzoate or petroleum ether have been prepared in this way. While the primary-valence theory of polymerization accounts for most classes of resin gelation, it is possible that in some instances the process must be attributed to association through secondary valences.

#### OXIDIZING ALKYDS AS PAINT VEHICLES

Comparison of drying alkyd type compositions with quick-drying paints (based on bodied tung oil-linseed oil mixtures) indicates that the widest application of the former may be in solid colors, but adverse aging phenomena show the need for precautions in manufacturing such colors.<sup>16</sup>

Schmutz, Palmer and Kittelberger,<sup>17</sup> studying the abnormal failure of paints due to poor bonding between the paint and the wood, have found that varnish in the priming coat affords much greater adhesion than the customary vehicles, regardless of the type of pigment used. A 100 per cent synthetic resin varnish as primer showed very favorable properties, though surpassed by 100 per cent spar varnish.

Mileti and Eddy<sup>18</sup> state that alkyd resin paints give an appearance superior to that of linseed oil paints, but are harder to apply. The linseed oil paints are exceeded in durability only by the paints derived from soft alkyd resins. The volume ratio of pigment had no influence upon durability, but only small amounts of basic pigments (e.g., zinc oxide) should be incorporated in alkyd paints to avoid livering. White and light-tinted alkyd paints are said to have a tendency to chalk, which may limit the use of alkyd resins as a paint vehicle to paints containing unreduced colored pigments.<sup>19</sup> Antimony oxide appears to be the best pigment when an alkyd resin paint is to be tinted. The resulting paint is equal to standard linseed oil paint.<sup>20</sup>

Gardner and Hart in a series of tests on quick-drying, faintly tinted house paints found that linseed oil paints did not possess as good color-retention as

<sup>15</sup> R. H. Kienle, *Ind. Eng. Chem.*, 1931, 23, 1260.

<sup>15a</sup> See Chapter 4.

<sup>16</sup> H. A. Gardner and L. P. Hart, *Circ. Am. Paint, Varnish Mfrs. Assn.*, 1932, 406, 11; *Brit. Chem. Abs. B*, 1933, 29.

<sup>17</sup> F. C. Schmutz, F. C. Palmer and W. W. Kittelberger, *Ind. Eng. Chem.*, 1930, 22, 855.

<sup>18</sup> O. Mileti and P. S. Eddy, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1933, 423; *Chem. Abs.*, 1933, 27, 432.

<sup>19</sup> H. A. Gardner and L. P. Hart, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1932, 420, 378; *Chem. Abs.*, 1933, 27, 198. See also *Circ., Nat. Paint, Varnish and Lacquer Assoc.*, 1934, 471, 339; *Chem. Abs.*, 1935, 29, 359.

<sup>20</sup> *Circ. Nat. Paint Varnish, and Lacquer Assoc.*, 1934, 471, 339; *Brit. Chem. Abs. B*, 1935, 31.

glycerol-phthalate vehicles.<sup>21</sup> These workers also noted that alkyd coatings chalked less but that some cracked more than bodied tung oil finishes.<sup>22</sup> Further experiments by Gardner and Hart<sup>23</sup> on quick-drying house paints gave good results. A number of mixtures of white lead, zinc oxide, and titanium oxide with a glycerol-phthalic anhydride vehicle successfully withstood exposure to the weather.

When there is a higher-boiling solvent in the diluent, the alkyd resin forms a harder film. However, with a slow evaporation rate the film has an opportunity to oxidize considerably. If certain solvents (e.g., petroleum hydrocarbons) are still present by the time the film has partially oxidized, precipitation and consequent loss of gloss may occur. This may be prevented by addition of eugenol, creosol, or guaiacol as oxidation inhibitors.<sup>24</sup> The addition of 1 per cent of benzoic, salicylic or  $\alpha$ -crotonic acids to linseed oil paint, a four-hour enamel and a bodied oil enamel<sup>25</sup> led to an increase in gloss, the effect being greatest with benzoic acid. However the influence of the acids upon skinning, settling, and yellowing of the film was not uniform.

Hardening of oxidizing alkyd resins, like that of drying oils, is accelerated by metallic driers. These are added in the form of solutions of metallic soaps (linoleates or naphthenates) in mineral spirits or turpentine.<sup>26</sup> Compositions containing driers should not be cooked with the phthalic resins as insoluble compounds are formed. Resinate driers tend to reduce elasticity and durability, and cause greater yellowing of the film than do the linoleate types. Different metals vary in their drying effects, thus zinc has a hardening effect, and may be used in combination with cobalt in baking enamels to secure good drying without surface wrinkling.

Alkyd resins are usable as vehicles for the preparation of rust-preventing paints by incorporation with certain pigments. A study of rust-inhibitive primers on steel panels over a period of 3 months showed the alkyd-zinc chromate formulation to be best.<sup>27</sup> The use of an alkyd resin modified by drying oils as the undercoat has been proposed<sup>28</sup> for places where nitrocellulose lacquers are to be the final coat. White lead, red lead, basic lead chromate and zinc chromate are mentioned as good pigments for these primers.<sup>29</sup>

Coating compositions suitable for intermediate coats on automobile bodies have been made, using pigments and a polymerized binder of the drying-alkyd type.<sup>30</sup> When the oil content is not less than 23 per cent, the resin may be used as a binder in a coating composition for the application of a plurality of coats which dry as a unit. There is no intermediary baking; a certain time is allowed, however, to permit the volatile solvents of one coat to evaporate before the next coating is applied. All the coats dry in a single baking operation to a state which

<sup>21</sup> H. A. Gardner and L. P. Hart, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1932, 422, 289; *Brit. Chem. Abs. B*, 1933, 1018.

<sup>22</sup> H. A. Gardner and L. P. Hart, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1933, 436, 226; *Brit. Chem. Abs. B*, 1933, 1067.

<sup>23</sup> H. A. Gardner and L. P. Hart, *Circ., Nat. Paint, Varnish and Lacquer Assoc.*, 1934, 467, 151; *Brit. Chem. Abs. B*, 1934, 771. L. P. Hart and H. A. Gardner, *ibid.*, 1935, 481, 159; *Chem. Abs.*, 1935, 29, 4189.

<sup>24</sup> J. W. Iliff and H. R. Young, U. S. P. 1,942,757, Jan. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1880. G. R. Greensback (U. S. P. 1,898,363, Feb. 21, 1933; *Chem. Abs.*, 1933, 27, 2659) retards the rancidity in fats, oils and fatty acids by use of maleic, aconitic, fumaric, itaconic or itaconic acids, esters or anhydrides. The addition of 0.01 per cent is effective in certain instances.

<sup>25</sup> H. A. Gardner and G. G. Sward, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1931, 401, 388; *Chem. Abs.*, 1932, 26, 607.

<sup>26</sup> J. McE. Sanderson, *Paint, Oil, Chem. Rev.*, 1932, 93 (22), 18; *Chem. Abs.*, 1932, 26, 4188.

<sup>27</sup> *Circ. Am. Paint, Varnish Mfrs. Assoc.*, 1933, 445, 469; *Brit. Chem. Abs. B*, 1934, 71. See however *ibid.*, 1934, 471, 343; *Chem. Abs.*, 1935, 29, 361.

<sup>28</sup> H. H. Hopkins, U. S. P. 1,771,538, July 29, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 24, 4647. *British P.* 297,418, 1928; *Chem. Abs.*, 1929, 23, 2841. See also K. Ott and H. Bernard, *German P.* 533,512, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5776.

<sup>29</sup> G. H. Eslinger, *Canadian P.* 327,522, 1932, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 1218.

<sup>30</sup> *British P.* 344,271, 1939, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 4190. See also M. J. Callahan, U. S. P. 2,006,068, May 28, 1933.



permits sanding.<sup>31</sup> A ground coat of vitreous enamel on steel or iron forms a good primer upon which to apply synthetic resin enamels.<sup>32</sup> Metal used in the construction of cans may be coated with an alkyd resin composition, it being possible to bake the coat on the metal before the cans are constructed.<sup>33</sup> A wire-enamel, said to form a uniform film quickly, is obtained by dissolving an alkyd resin in a hydrogenated petroleum product.<sup>34</sup>

Oil paints may be improved by having 10 per cent oil-soluble alkyd resin incorporated in them.<sup>34</sup> Coating compositions for outside use, of high durability and having a high percentage of pigment, have been made by employing alkyds of low acid number.<sup>35</sup> Thus a resin of acid number 2.5 is made from 13.43 parts of glycerol, 72.06 parts of linseed oil acids and 14.51 parts of phthalic anhydride. One hundred parts of resin are used with 101 parts of barium-base titanium oxide pigment, 39.4 parts of lithopone, 15.6 parts of zinc oxide, 0.8 part of cobalt-manganese drier and 62 parts of mineral spirits thinner. Other mixed or single pigments and variations in the composition of the resins may be introduced. The chalking-tendency of the titanium oxide is considerably reduced, allowing its use as a chief pigment.

Antimony oxide in mixed-pigment paints of this kind<sup>36</sup> eliminates the chalking tendency, permitting the formulation of non-fading colored titanium oxide coating compositions. Barium titanate used as a pigment in these compositions has good binding power.<sup>37</sup> By lowering the acid number of the alkyd, zinc oxide may be used as the principal pigment constituent.<sup>38</sup> With resins containing less than 35 per cent of drying oil acids, the acid number should be below 30. Highly leaded zinc oxides in Rezyl vehicles are said to have unusual gloss-retention.

As has been stated in Chapter 47, alkyd resins in cellulose ester compositions protect the latter from the discoloring effects of ultraviolet light. This principle has been applied to the production of non-discoloring sheets of pyroxylin plastic compositions. Both sides of the plastic are coated with a transparent oil-resin varnish for the purpose of absorbing actinic rays.<sup>39</sup> Sheets of cellophane may be bonded by an alkyd resin and coated with an insulating varnish to produce an electric-insulating material.<sup>40</sup> An alkyd resin, modified by perilla oil, applied to cellophane forms a base upon which a moisture-proof coating can be applied.<sup>41</sup>

Water paints containing an oily alkyd resin modified with linseed oil acids were proposed by Ott and Breyer.<sup>42</sup> The resin was mixed with ferric oxide and emulsified in water containing casein, ammonia and borax.

Light-colored coating compositions have been produced from oil-modified alkyd

<sup>31</sup> R. A. Jacobson and J. L. Keats, U. S. P. 1,912,369, 1,912,370, 1,912,371, 1,912,372, June 6, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 4430.

<sup>32</sup> F. C. Zimmer, U. S. P. 1,930,331, Oct. 10, 1933, to General Electric Co.; *Chem. Abs.*, 1934, 28, 390.

<sup>33</sup> H. H. Hopkins, British P. 297,418, 1928, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1929, 23, 2841. See also C. B. Hemming and E. C. Pitman, U. S. P. 1,999,413, Apr. 30, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 3972.

<sup>34</sup> W. H. Wright, U. S. P. 1,977,932, Oct. 23, 1934, to Schenectady Varnish Co.; *Chem. Abs.*, 1935, 29, 366.

<sup>35</sup> German P. 578,469, 1933 to Firma L. Blumer; *Chem. Abs.*, 1933, 27, 4427.

<sup>36</sup> W. W. Lewers and G. D. Patterson, U. S. P. 1,885,024, Oct. 25, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1215.

<sup>37</sup> G. D. Patterson, U. S. P. 1,885,025, Oct. 25, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1215. See also work of H. A. Gardner and L. P. Hart, *loc. cit.*

<sup>38</sup> G. D. Patterson, U. S. P. 1,885,026, Oct. 25, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1215. For further work on titanium pigments see H. H. Hopkins and F. S. Stewart, U. S. P. 1,933,460, Dec. 4, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 637.

<sup>39</sup> G. D. Patterson, U. S. P. 1,885,027, Oct. 25, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1215.

<sup>40</sup> J. H. Clewell, Jr., Canadian P. 310,844, 1931, to Canadian Industries, Ltd.

<sup>41</sup> C. F. Obermaier, British P. 409,803, 1932, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B, 1934, 537.

<sup>42</sup> W. H. Charch, W. L. Hyden and J. C. Siemann, U. S. P. 1,972,869, Sept. 11, 1934; *Chem. Abs.*, 1934, 28, 7013.

<sup>43</sup> K. Ott and B. Breyer, German P. 599,311, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6001.

resins with an organic peroxide as drier.<sup>43</sup> The oil glyceride present in the resin should not exceed 65 per cent, if slow drying is to be avoided. Treatment of lithopone with acetic acid prevents thickening of enamels made from oil-treated alkyds.<sup>44</sup>

Resins modified with a large proportion of linseed oil acids or other drying oil acids have been applied to the preparation of white enamels,<sup>45</sup> in conjunction with low-viscosity nitrocellulose. Alkyd resins in striping enamels contain more than 50 per cent of drying oil fatty acids.<sup>46</sup>

Leather can be finished off with an oil-modified Glyptal; it is first coated with a mixture of bodied linseed oil in which is incorporated pigments. This is followed by coats of bodied linseed oil thinned with naphtha and then the final coat of resin is dried on at 150-175°F. for 10-20 hours.<sup>47</sup> A varnish for flexible floor coverings can be made by heating a drying-oil resin with a bodied drying oil.<sup>48</sup> A proposed high-glaze finish for fabrics consists of drying oils with a polyhydric alcohol-polybasic acid resin, driers, and a solvent (toluol). This final coating is applied over a cellulose nitrate undercoat.<sup>49</sup>

Coating or finishing compositions for rubber or rubberized cloth<sup>50</sup> have been prepared from alkyd resins modified with drying, semi-drying or fatty oils (e.g., castor oil) or the acids produced on their hydrolysis. Phenol-formaldehyde resins, cellulose esters and plasticizers may be added. Likewise a drying oil-modified alkyd resin-asphalt varnish has been suggested for the purpose.<sup>51</sup> Another use of this varnish is its application to uncured rubber which is then baked to secure an artificial leather.<sup>52</sup> Alkyd resins modified with boiled tung oil may be employed in crystallizing-varnishes for the production of frosted films.<sup>53</sup>

Alkyd resins containing at least one free hydroxyl group and which dissolve or swell strongly in benzene hydrocarbons may be admixed with cellulose ethers to give varnishes or mastics.<sup>54</sup> Thus ethyl cellulose, and the condensation product of phthalic acid and linoleic glyceride, containing unesterified groups, are dissolved in a benzene-toluene-alcohol mixture, yielding a varnish which is a prospective coating for wood. The alkyd resins modified with a monobasic acid (e.g., linseed oil acid), but containing no excess of the acid, are employed for the production of varnishes.<sup>55</sup> Incorporation of 5 per cent  $\alpha$ -unsaturated aliphatic carboxylic acids

<sup>43</sup> P. Robinson and B. E. Sorensen, U. S. P. 1,989,711, Feb. 5, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 2376. Canadian P. 325,404, 1932, to Canadian Ind., Ltd.; *Chem. Abs.*, 1932, 26, 5777.

<sup>44</sup> G. D. Patterson, U. S. P. 1,889,130, Nov. 11, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.*, 1933, 721.

<sup>45</sup> E. F. Arnold, British P. 350,463, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 2071. For a review of white enamels from alkyd resins see *Chemical Industries*, 1934, 34, 417.

<sup>46</sup> E. F. Arnold, Canadian P. 310,845, 1931, to Canadian Ind., Ltd.; *Chem. Abs.*, 1931, 25, 3184.

<sup>47</sup> H. H. Hopkins, U. S. P. 1,954,750, Apr. 10, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3838. British P. 334,000; *Chem. Abs.*, 1934, 28, 385. See also U. S. P. 1,959,363 and 1,960,220, May 22, 1934; *Brit. Chem. Abs.*, 1935, 320.

<sup>48</sup> W. F. Whitecarver and H. H. Hopkins, U. S. P. 1,942,736, Jan. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1589. Canadian P. 331,451, 1933, to Canadian Ind., Ltd.; *Chem. Abs.*, 1933, 27, 3896. British P. 398,209, 1933; *Chem. Abs.*, 1934, 28, 1557. See also P. H. Pennell and C. H. Draper, U. S. P. 1,968,959, Jan. 22, 1935, to Armstrong Cork Co.; *Chem. Abs.*, 1935, 29, 2005.

<sup>49</sup> A. W. Battman and R. E. Thomas, U. S. P. 1,954,751, Apr. 10, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.*, 1935, 145.

<sup>50</sup> R. Hill and E. E. Walker, British P. 330,949, 1928, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1930, 24, 6041.

<sup>51</sup> H. J. Barrett, U. S. P. 1,995,957, Mar. 26, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 3428. British P. 388,746, 1933; *Chem. Abs.*, 1933, 27, 4939.

<sup>52</sup> A. J. Hemmer, U. S. P. 1,944,709, Nov. 14, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 938. British P. 390,828, 1933; *Chem. Abs.*, 1933, 27, 6013. See also A. F. Alvardo and A. N. Perrett, U. S. P. 1,955,355, April 17, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3921. Canadian P. 331,634, 1933, to Canadian Ind., Ltd.; *Chem. Abs.*, 1933, 27, 3836. J. R. Couture, U. S. P. 1,936,500, Nov. 21, 1933, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.*, 1934, 797. H. J. Barrett, Canadian P. 331,635, 1933, to Canadian Ind., Ltd.; *Chem. Abs.*, 1933, 27, 3836.

<sup>53</sup> W. O. Stauffer, U. S. P. 1,944,835, Apr. 17, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.*, 1935, 144. Canadian P. 310,846, 1931, to Canadian Ind., Ltd.; *Chem. Abs.*, 1931, 25, 3184. British P. 350,641, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 8124.

<sup>54</sup> French P. 657,116, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 838.

<sup>55</sup> K. Ott, H. Bernard and F. Frick, Canadian P. 308,131, 1931, to I. G. Farbenind. A.-G.

(e.g., crotonic or sorbic acid) improves the flowing qualities.<sup>56</sup> Drying alkyds may be dissolved and mixed with colors to form fast-drying inks for offset or intaglio printing.<sup>57</sup> A glycerol-phthalic anhydride drying-oil resin has been utilized in making printing enamel.<sup>58</sup>

Adams<sup>59</sup> described the preparation of metallic paints by suspending metal powders (such as aluminum, copper alloys or silver) in a vehicle consisting of a drying alkyd in a volatile solvent. Paints containing zinc or aluminum may be applied to metals (e.g., iron or copper) and alloy formation effected by heating the metal surface. Metallic flakes in quick-drying varnishes composed of an alkyd resin modified by linseed and tung oils have improved "leafing" properties.<sup>60</sup>

Laborious finishing processes whereby spray-coated articles must be sanded by hand and finished with a spray mist of lacquer thinner may be obviated by subjecting the film to heat so that abrasive marks will be eliminated. The film should contain substances softening under heat-treatment without harmful physical alteration, so that surface flowing is achieved. The presence of oxygen leads to oxidation and subsequent hardening of the film. Lacquers containing drying alkyds are suitable for such treatment, the sanded film being heated at 70-120°C. An example of a suggested composition contains 1.82 per cent nitrocellulose, 23.27 per cent glycerol-phthalic-linseed oil acid resin, 0.91 per cent carbon black pigment, and 74.00 per cent lacquer thinner.

A non-caking pigmented coating can be prepared from a pigment ground in a gasoline solution of rubber to which an alkyd-type resin has been added.<sup>61</sup> Root<sup>62</sup> suggested that a phthalic anhydride-glycerol-linseed oil resin be employed in coating compositions for producing wrinkled finishes on metal. In this type of varnish, it has been generally considered essential to use a varnish resin in a drying oil that will wrinkle on oxidation. However, by using an alkyd resin modified with linseed oil acids, the resin needs only to be dissolved in volatile solvents (e.g., toluol, xylol, naphtha) to give a composition that wrinkles upon baking.

<sup>56</sup> H. Bernard, U. S. P. 1,833,274, Nov. 24, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 807.

<sup>57</sup> British P. 337,199, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2011. French P. 700,892, 1929; *Chem. Abs.*, 1931, 25, 3855.

<sup>58</sup> E. H. Callahan, Canadian P. 332,858, 1933, to Canadian Industries, Ltd.; *Chem. Abs.*, 1933, 27, 4428.

<sup>59</sup> L. V. Adams, British P. 337,652, 1929, to British Thomson-Houston Co.; *Chem. Abs.*, 1931, 25, 2310. Canadian P. 313,728, 1931, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1931, 25, 5304.

<sup>60</sup> J. W. Iliff and P. Robinson, U. S. P. 1,941,398, Dec. 26, 1933; *Brit. Chem. Abs. B*, 1934, 849; British P. 396,081, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1933, 837. H. H. Hopkins and J. Richardson, Jr., U. S. P. 1,967,936, July 24, 1934; *Chem. Abs.*, 1934, 28, 6001.

<sup>61</sup> C. Coolidge and H. S. Holt, U. S. P. 1,863,834, June 21, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1933, 479.

<sup>62</sup> F. B. Root, U. S. P. 1,976,191, Oct. 9, 1934, to Chadeloid Chem. Co.; *Chem. Abs.*, 1934, 28, 7562.

## Chapter 49

### Alkyd Resins in Molding Compositions

Alkyd resins are much less widely employed as binders to form molded articles than in coating compositions. The reason for this is that conversion to the infusible insoluble form is very slow in comparison with the transformation of other synthetic resins generally used for this purpose (urea-formaldehyde and phenol-formaldehyde). Also, since the hardening reaction is probably one of further interesterification of the molecules of the intermediate resin, considerable water vapor is evolved, which tends to form bubbles in the mass. In thin films (e.g., baked coatings) the water readily escapes and high temperatures can be used without disrupting the physical continuity of the resin layer, but in massive form heating must be carried out at a low temperature to allow slow diffusion of water vapor. This low-temperature curing requires inordinately long baking periods<sup>1</sup> and limits the use of heat-hardening alkyd resins to certain special fields where particular properties of the hardened resin give it a distinct advantage.

With alkyd resins of the fusible soluble variety the same considerations hold in regard to their use in molded materials. They must compete with cheaper thermoplastic substances and consequently are successfully used from an economic standpoint only in applications where some particular property of the resins comes into play (e.g., high compatibility with nitrocellulose).

It is possible to accelerate the transformation to the infusible form. For example, a mixture of three mols of phthalic anhydride and two mols of glycerol is suddenly transformed at 235-240°C. from a liquid to a spongy solid, which is quite insoluble in ordinary solvents. A number of substances (e.g., zinc oxide, calcium oxide, barium carbonate or barium hydroxide) lower the temperature at which solidification occurs.<sup>2</sup> This result is probably due to the phthalate salt formed.<sup>3</sup> Ammonium persulphate also has a marked catalytic action on the solidification step. For example, an agitated mixture of 2.7 parts of phthalic anhydride and 1 part of glycerol would normally solidify at 235-240°C. but, if ammonium persulphate is added to the batch held at 140-145°C., the mass becomes too viscous to be stirred. Bleaching powder causes conversion of the same phthalic anhydride-glycerol mixture at 165°C. Uranium nitrate, ammonium bisulphate or zinc chloride yielded a rubbery compound at 155°C.

Silicotungstic acid in the proportion of 10 per cent exerts a vigorous action at 115-125°C.; 4 per cent of this compound brings about solidification at 155°C. A resin, prepared from equimolecular proportions of glycerol and phthalic anhydride but heated only to 232°C. to avoid transformation to the insoluble heat-resistant form, was found to harden quickly on the hot plate after admixture

<sup>1</sup> To obtain light-colored slabs of phthalic anhydride-glycerol resins free of bubbles, J. H. Schmidt (U. S. P. 1,663,133, Mar. 20, 1928, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 1696) found it necessary to subject the initial reaction product to a temperature of 125° C. for a period of several weeks.

<sup>2</sup> Carleton Ellis, U. S. P. 1,897,977 and 1,897,978, Feb. 14, 1933, to Ellis-Foster Co.; *Brit. Chem. Abs. B*, 1933, 978.

<sup>3</sup> It is noteworthy in this connection that the addition of soaps in small proportions (0.1 per cent), especially the fatty acid salts of aluminum, tin, zinc and magnesium, accelerates the esterification of higher fatty acids with polyhydric alcohols. British P. 302,411, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 235.

with silicotungstic acid. Wright<sup>4</sup> added dehydration catalysts (e.g., oxides of calcium, magnesium and zinc or finely divided iron and zinc) to aid the transformation to an infusible stage.

#### MOLDED PRODUCTS

The general properties of alkyd resins have led to efforts to utilize them in the manufacture of molded products. One method makes use of a resin prepared from glycerol and one or more polybasic acids, with cellulose esters or cellulose ethers for strengthening and toughening the products.<sup>5</sup> Resins may be obtained, for example, by heating a mixture of glycerol, salicylic acid and phthalic anhydride to a temperature of approximately 290°C. The temperature is raised slowly, and the product is cooled under reduced pressure to remove as much as possible of unused acid. This treatment also aids in the production of light-colored resins.

Generally the acid number of a resin should be as low as 20 if nitrocellulose is to be incorporated, and this can be obtained by the use of excess glycerol, by protracted heating at 200-300°C. or by adding an aromatic amine (aniline or toluidine).<sup>6</sup> In addition to nitrocellulose, the resin may be mixed with fillers (e.g., lampblack, asbestos, mica dust). The compositions are rendered plastic by warming, placed in a mold and pressed while chilling.<sup>7</sup> The following example illustrates the proportions employed:

	Parts by Weight
Mica dust . . . . .	12
Terra alba . . . . .	8
Rosin phthalic glyceride resin . . . . .	8
Nitrocellulose . . . . .	2
Asbestos fiber . . . . .	1
Lampblack . . . . .	1

Nitrocellulose, up to 10 per cent, increases the strength of the final product but further additions do not give proportionate results.

Cold-molded articles may be produced from a mixture of asbestos fiber and other mineral fillers with an alkyd resin. The addition of 1-2 per cent of a drying oil (tung oil) is advantageous. The cold-molded article is air-dried for 24 hours, after which the temperature is raised to 70°C. for 5-6 hours. It is then baked for 30 minutes at 150-180°C. and finally at 290-300°C. for 0.5-1 hour. A typical resin for use in this connection is made by heating 100 parts of rosin, 21 parts of phthalic anhydride and 24 parts of glycerol at 280-290°C. The phthalic anhydride may be replaced by citric, tartaric, malic, maleic or succinic acids, or their anhydrides.<sup>8</sup>

Wright<sup>9</sup> produced a molding composition by heating the alkyd resin already in the B stage with a swelling agent (e.g., acetone) in the presence of a plasticizer (e.g., vinyl chloride or tolyl phosphate). Extrudable compositions may be formed by working between hot rollers a mixture of 3 parts of the totally cured resin and 1 part of the same resin in the uncured or semi-cured state.<sup>10</sup> Zinc oxide or other basic materials hasten the curing process.

<sup>4</sup> J. G. E. Wright, U. S. P. 1,581,902, Apr. 20, 1926, to General Electric Co.; *Chem. Abs.*, 1926, 20, 1913. British P. 236,591, 1925, to British Thomson-Houston Co., Ltd.; *J.S.C.I.*, 1925, 44, 770B. German P. 555,534, 1925, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1925, 26, 6167.

<sup>5</sup> Carleton Ellis, U. S. P. 1,876,886, Sept. 13, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 200.

<sup>6</sup> See also Carleton Ellis, U. S. P. 1,843,869 and 1,843,870, Feb. 2, 1932, to Ellis-Foster Co.; *Brit. Chem. Abs. B*, 1932, 1042.

<sup>7</sup> Carleton Ellis, U. S. P. 1,876,886, Sept. 13, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 200.

<sup>8</sup> Carleton Ellis, U. S. P. 1,541,836, June 9, 1925, to Ellis-Foster Co.; *Chem. Abs.*, 1925, 19, 3277.

<sup>9</sup> J. G. E. Wright, British P. 294,450, 1932; *Brit. Chem. Abs. B*, 1933, 721. French P. 733,836, 1932, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 27, 1221.

<sup>10</sup> M. M. Safford, U. S. P. 1,975,750, Oct. 2, 1934, to General Electric Co.; *Chem. Abs.*, 1934, 28, 7394. British P. 396,354, 1933, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1934, 28, 664. French P. 43,508, 1934, addn. to 701,429, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1935, 29, 854.

## MOLDED MICA PRODUCTS

The excellent electrical resistance of sheet mica combined with high mechanical strength and heat-resistant properties has resulted in its use in the manufacture of electrical machinery from the earliest days of the industry. The scarcity of large sheets of mica and the high price of such material have given rise to the development of a large industry for the manufacture of composite sheets from flake mica, mica waste, split mica and mica powder, since these materials are abundant and cheap.<sup>11</sup>

An early method of producing composite mica sheets was developed by Lee.<sup>12</sup> He incorporated the mica with shellac by heating. Dyer<sup>13</sup> used shellac varnish for this purpose. Flakes are coated with varnish, allowed to dry and pressed together under heat. When used in commutator construction, mica plates or cones are liable to become sufficiently heated for shellac to soften, which causes carbonization and short circuits. Attempts to overcome this difficulty by the use of phenol-aldehyde resins have shown that these also carbonize readily and, moreover, they do not adhere well to mica. Alkyd resins, on the other hand, appear to satisfy the requirements of a bonding agent for mica and have been used for this purpose. Such mica compositions have a high electrical strength, the value for alkyd composite sheets being higher than for shellac-bonded mica. The power factor (see Chapter 69) of properly made alkyd-cemented mica at 100 kilocycles is given as 1.95, as compared with 4.6 for the shellac-bonded product.<sup>14</sup> Properly cured alkyd-treated sheets yield less under mechanical compression and are more flexible than the shellac-bonded material.

Barringer and Peterson<sup>15</sup> prepared a laminated mica product by treating mica flakes or plates with an acetone solution of the alkyd resin, evaporating the solvent and heating the composition at 175°C. until the binder is in an intermediate plastic state. The product then is molded at 250°C., hardened at 300°C. and cooled under pressure. The procedure may be modified<sup>16</sup> by carrying out the first stage of the curing under reduced pressure to facilitate removal of solvent and volatile reaction products. Mica plates are pasted together as before with the solution of an alkyd resin in acetone. The built-up sheets are covered on both sides with dry mica to prevent sticking to the supports and are heated in an evacuated oven at 110°C. for 0.5-2 hours. Acetone is completely removed in the process and some preliminary polymerization of the resin occurs. During further curing of the material at 160-170°C. an intermittent pressure is applied, the release of the pressure providing for the escape of evolved gases. The final heat treatment is carried out as described above.

Coffey<sup>17</sup> found that thin mica splittings can be cemented together with a condensation product of glycerol and phenol and molded under pressure. Five parts by weight of the resin are used with 95 parts of mica. The hot material may be molded into shapes which retain their form when cooled. Coffey also described a commutator ring the outer layer of which consists of mica plate prepared by cementing mica flakes with alkyd resin, and the inner layer composed of asbestos impregnated with shellac.<sup>18</sup> Asbestos gives to the material a certain resiliency

<sup>11</sup> A historical survey of the early development in this field is given by J. Roseman, *Plastics*, 1928, 4, 549.

<sup>12</sup> C. T. Lee, U. S. P. 389,519, Sept. 11, 1888. British P. 9227, 1889; *J.S.C.I.*, 1889, 8, 781.

<sup>13</sup> A. H. S. Dyer, U. S. P. 452,646, Oct. 4, 1892. British P. 10,524, 1892; *J.S.C.I.*, 1892, 12, 527.

<sup>14</sup> H. Warren, *Electrician*, 1927, 98, 286; *Chem. Abs.*, 1928, 22, 2281.

<sup>15</sup> L. E. Barringer and C. F. Peterson, U. S. P. 1,589,004, June 18, 1926; *Chem. Abs.*, 1926, 20, 3065. British P. 203,332, 1922, to British Thomson-Houston Co., Ltd.; *J.S.C.I.*, 1923, 42, 1031A.

<sup>16</sup> L. E. Barringer and C. F. Peterson, U. S. P. 1,619,692, March 1, 1927, to General Electric Co.; *Chem. Abs.*, 1927, 21, 1336. British P. 250,942, 1925, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1927, 21, 1337. C. F. Peterson, U. S. P. 1,619,753, March 1, 1927, to General Electric Co.; *Chem. Abs.*, 1927, 21, 1336.

<sup>17</sup> J. M. Coffey, U. S. P. 1,945,415, Oct. 11, 1927, to Mica Insulator Co.; *Chem. Abs.*, 1928, 22, 128. Canadian P. 283,428, 1928; *Chem. Abs.*, 1928, 22, 4157. British P. 288,360, 1927; *Chem. Abs.*, 1928, 22, 656.

<sup>18</sup> J. M. Coffey, U. S. P. 1,857,586, May 10, 1932, to Mica Insulator Co.; *Chem. Abs.*, 1932, 26, 3860.

which causes the ring to conform more readily to irregularities in shape of the commutator copper bars, and thus permits a tight connection.

Frederick<sup>19</sup> used both shellac and alkyd resin in making mica sheets. The sheet is formed from a mixture of mica with shellac and then coated with an alkyd resin. The whole mass is subjected to heat to amalgamate the shellac with alkyd resin and to change the latter to the infusible state.

Single sheets of mica may be covered with a mixture of an alkyd resin and a vapor-adsorbing filler (e.g., asbestos, iron oxide, kieselguhr or talc) and then the resin is hardened by heating under pressure.<sup>20</sup> Insulators are made by cementing sheets of mica with a resin prepared from polyhydric alcohols and dicarboxylic acids of the type of diglycolic.<sup>21</sup> The resin derived from glycerol and phthalic anhydride modified with drying oil, or drying oil acids, may be used.<sup>22</sup> Weber suggested bonding mica flakes with a mixture of an alkyd resin, an aromatic phosphate plasticizer and a glue.<sup>23</sup> The composite article is consolidated by heating under pressure at 250°C.<sup>24</sup>

#### FLOOR AND WALL COVERINGS

The addition of alkyd resins to flooring compositions has been proposed because the resins form flexible final products. Increased flexibility in a floor covering would mean that such rugs would lie flatter. One application of this type<sup>25</sup> relates to a duplex floor covering consisting of a saturated felt base and a tread-veneer of resin-nitrocellulose composition. The plastic coating compositions are obtained by dissolving nitrocellulose, alkyd resin and plasticizing materials in volatile solvents. The product is mixed with ground cork and fireproofing agents (e.g., powdered gypsum or magnesium carbonate). This agglomeration is put through a sheeting machine, deposited on the felt and dried.

One resin that may be used in the coating composition is prepared by heating to 290°C. a mixture of rosin (100 parts), phthalic anhydride (50 parts) and glycerol (48 parts). The following formula will illustrate the type of composition and proportions by weight: nitrocellulose (40 parts), rosin ester (40 parts), castor oil (58 parts), tricresyl phosphate (15 parts), powdered gypsum (300 parts), ground cork (100 parts), pigment (10 parts) and solvent (80 parts). Volatile solvents (acetone, methyl alcohol or isopropyl alcohol) that do not dissolve the asphalt of the felt are preferable.<sup>26</sup>

If a thicker product is desired more layers of tread can be added to the covering. When high-boiling solvents are used in conjunction with multiple layers, the time of drying is increased to the point where the cost of manufacture would be high. On the other hand, employment of volatile solvents alone results in rapid evaporation during the sheeting process. To make possible the use of volatile solvents, wax (e.g., paraffin, carnauba or montan) is added to the flooring composition. This retards evaporation at room temperatures without interfering with

<sup>19</sup> L. T. Frederick, U. S. P. 1,873,753, Aug. 23, 1932, to Continental Diamond Fibre Co.; *Chem. Abs.*, 1932, 26, 6083.

<sup>20</sup> British P. 329,878, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5952. French P. 679,596, 1929; *Chem. Abs.*, 1930, 24, 3893.

<sup>21</sup> French P. 696,196, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2823.

<sup>22</sup> E. M. Hansheer, British P. 366,354, 1931, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B, 1932, 353. French P. 715,063, 1931, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 1693.

<sup>23</sup> H. C. P. Weber, U. S. P. 1,928,718, March 10, 1933, to Westinghouse Elec. and Mfg. Co.; *Chem. Abs.*, 1933, 27, 5847.

<sup>24</sup> C. D. Hoeker (U. S. P. 1,512,024, Oct. 21, 1925; *Chem. Abs.*, 1925, 19, 710) obtained a moldable composition for electrical insulation by mixing mica with the reaction product formed by heating castor oil to the point of partial carbonization. In place of castor oil other substances capable of yielding glycerol and an organic acid were suggested.

<sup>25</sup> Carleton Ellis, U. S. P. 1,784,135, Dec. 9, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 435.

<sup>26</sup> For the inclusion of alkyd resins in flooring compositions for use with paper base see Carleton Ellis, U. S. P. 1,784,799, Dec. 9, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 435.

the final drying operation. The wax also facilitates the printing of a design on the surface of the floor covering.<sup>27</sup>

The inclusion of lithopone, white lead, lead sulphate, baryta and chalk in the alkyd-nitrocellulose coating produces a white finish. Small masses of intense colors introduced onto the white sheeting yield variegated color effects, and cotton linters incorporated into the surface give a white textured effect.<sup>28</sup>

Nitrocellulose and wax are considered to be incompatible but Lougovoy<sup>29</sup> has developed a nitrocellulose tread coating which adhered well to paper waterproofed with a high proportion of wax. The following example will serve to illustrate the type of composite utilized:

	Parts by Weight
Cleaned motion-picture film . . . . .	200
Acetone . . . . .	300
Benzol . . . . .	150
Tricresyl phosphate . . . . .	130
Blown castor oil . . . . .	130
Denatured alcohol . . . . .	50
Paraffin wax . . . . .	10
Benzoic-phthalic-glyceride resm . . . . .	60
Rosin . . . . .	40

This composition was thoroughly mixed and to it was added:

	Parts by Weight
Vegetable-ivory sawdust . . . . .	130
Wood flour . . . . .	100
Perhydrated calcium sulphate . . . . .	200
Lithopone . . . . .	200
Diphenylamine . . . . .	5
Pigment . . . . .	3

The plastic composition was sheeted onto a paper base containing paraffin wax.

The author<sup>30</sup> has also employed acetone-soluble cellulose acetate with alkyd resins to prepare a non-curling floor covering. The alkyd resins are incorporated with cellulose acetate, solvents, wax, fillers and pigments, and sheeted onto an asphalt-saturated felt base. The proportion of resin in this flooring composition should not exceed the proportion of cellulose acetate. The resins proposed<sup>31</sup> for use with nitrocellulose are linseed-phthalic glyceride, cottonseed-phthalic glyceride, blown rapeseed-phthalic glyceride, soya bean-phthalic glyceride, benzoic-phthalic glyceride and castor oil-glycerol or -glycol phthalate. The following example illustrates the preparation of these resins: Glycerol (94 parts by weight), phthalic anhydride (160 parts by weight) and fatty acids of linseed oil (80 parts by weight) are heated to 250°C. for two hours.

Phelan<sup>32</sup> has described an adhesive backing (for inlaid linoleum) prepared by coating a saturated felt base with an alkyd resin paint. The latter is made by heating at 150-180°C. a mixture of 35 parts of ethylene glycol, 3.5-7.5 parts of diethylene glycol, 8-13 parts of glycerol, 105 parts of phthalic anhydride and 30 parts of drying oil acids, and dissolving the product in ethylene glycol monoethyl ether. A floor-covering material is obtained by impregnating a felt base with a bituminous saturant, covering it with a sealing coat containing an alkyd resin and finally applying a decorative coating over the sealing coating. One advantage

<sup>27</sup> Carleton Ellis, U. S. P. 1,784,800 and 1,784,801, Dec. 9, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 425.

<sup>28</sup> Carleton Ellis, U. S. P. 1,784,802, 1,784,803 and 1,784,804, Dec. 9, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 425.

<sup>29</sup> B. N. Lougovoy, U. S. P. 1,784,805, Dec. 9, 1930, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 425.

<sup>30</sup> Carleton Ellis, U. S. P. 1,843,329, Mar. 8, 1932, to Rezyl Corp.; *Chem. Abs.*, 1932, 26, 2844.

<sup>31</sup> Carleton Ellis, U. S. P. 1,905,337, Apr. 25, 1933, to Rezyl Corp.; *Chem. Abs.*, 1933, 27, 3581. See Chapter 47 for illustrations of alkyd resins in nitrocellulose lacquers.

<sup>32</sup> J. A. Phelan, British P. 343,822, 1929, to Armstrong Cork Co.; *Chem. Abs.*, 1933, 27, 436.



of an alkyd resin is that it does not dissolve the bituminous material.<sup>33</sup> Sheet material, for floor coverings, gaskets and artificial leather, is obtained by felting together layers of comminuted cork or fibers that are saturated with an alkyd resin binder.<sup>34</sup>

#### ALKYD RESINS IN THE RUBBER INDUSTRY

During the process of vulcanization, the outer layer of rubber is likely to be overcured before the whole mass is vulcanized. This phenomenon is called scorching and is overcome in part by the addition of substances called scorch-retarders. The usefulness of alkyd resins as scorch-retarders has been investigated by Thies.<sup>35</sup> Glyceryl phthalate was an effective agent, but it interfered with curing if more than 0.25 per cent was added to the rubber. In such small amounts it is not as efficient as zinc resinate or benzoic acid.

Tendencies to pre-vulcanization, especially with accelerators of the 2-mercaptarylenethiazole type, are overcome by incorporating in the rubber mixture a condensation product of the polyhydric alcohol-polybasic aromatic acid class of acid value 100-150.<sup>36</sup> The resin not only modifies the rate of vulcanization but gives products which have satisfactory qualities with respect to aging, flexing and abrasion. It has also been found that the strength of vulcanized natural or synthetic rubber is enhanced by the addition of such resins.<sup>37</sup> The resistance of rubber to oil is increased by the incorporation of a large proportion of an alkyd resin.<sup>38</sup> The materials from which the alkyd resins are prepared may be added directly to a vulcanizable rubber mix.<sup>39</sup> A plastic rubber composition, which is resistant to hydrocarbons, is made by including an alkyd resin with the latex. The latex is mixed with the resin dissolved in 5 per cent ammonia, and the final product precipitated by the addition of acetic acid.<sup>40</sup>

Naunton and Siddle<sup>41</sup> report that lacquers prepared from alkyd resins are superior in several respects to nitrocellulose and oil varnishes for coating rubber goods. The film is hard, glossy and flexible and can be cold-vulcanized with sulphur monochloride. The gas-retaining property of heat-vulcanized rubber is improved by applying a composition composed of an alkyd resin, glycerol and gelatin. Alternatively, the rubber may be coated before vulcanization.<sup>42</sup>

Drummond<sup>43</sup> is of the opinion that alkyd resins last longer than rubber where exceptional resistance to heat and chemical action is required.

#### ELECTRICAL INSULATION

Laminated products for use in oil-filled electrical apparatus have been described by Segar.<sup>44</sup> The fibrous material is impregnated and bonded with a composition

<sup>33</sup> E. J. Pieper, British P. 349,792, 1929, to Armstrong Cork Co.; *Chem. Abs.*, 1933, 27, 436. See also E. J. Pieper, British P. 318,239, 1928, to Armstrong Cork Co.; *Chem. Abs.*, 1930, 24, 2317.

<sup>34</sup> British P. 399,856, 1933, to Behr-Manning Corp.; *Chem. Abs.*, 1934, 28, 1823.

<sup>35</sup> H. R. Thies, *Ind. Eng. Chem.*, 1931, 23, 1857.

<sup>36</sup> M. Jones and W. J. S. Naunton, U. S. P. 1,923,932, Aug. 22, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 5580. British P. 367,901, 1930; *Chem. Abs.*, 1933, 27, 2342. French P. 727,007, 1931; *Chem. Abs.*, 1932, 26, 5238.

<sup>37</sup> British P. 323,322, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1930, 205.

<sup>38</sup> W. J. S. Naunton, M. Jones and W. F. Smith, *Trans. Inst. Rubber Ind.*, 1933, 9, 169; *Brit. Chem. Abs. B.*, 1934, 212.

<sup>39</sup> D. F. Twiss and F. A. Jones, British P. 395,109, 1933, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1934, 28, 371.

<sup>40</sup> H. L. Grupe and R. H. Kienle, British P. 395,217, 1932, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B.*, 1933, 757. French P. 42,447, 1933, addn. to 683,772, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1934, 28, 1231.

<sup>41</sup> W. J. S. Naunton and F. J. Siddle, *India Rubber J.*, 1931, 82, 535, 561; *Chem. Abs.*, 1932, 26, 1151.

<sup>42</sup> A. E. T. Neale, E. W. B. Owen, J. A. Wilson and D. F. Twiss, British P. 416,679, 1934, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1935, 29, 1233. French P. 770,391, 1934, to Soc. anon. des pneumatique Dunlop; *Chem. Abs.*, 1935, 29, 643.

<sup>43</sup> A. A. Drummond, *Elec. Rev.*, 1928, 102, 59; *Chem. Abs.*, 1928, 22, 3397.

<sup>44</sup> H. D. Segar, U. S. P. 1,899,591, Feb. 23, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 3018.

containing equal parts by weight of shellac and an alkyd resin modified with drying oil acids.

A cable insulated with alkyd-treated cloth capable of resisting oil and withstanding high temperatures has been developed.<sup>43</sup> Although this cloth has a slightly lower dielectric strength than some varnish-treated cloth, its flexibility and toughness will cause it to retain its dielectric strength for a longer time. A suggested wrapping for rubber-coated wire consists of a fabric impregnated with diethylene glycol phthalate.<sup>44</sup>

By coating the outside of a structure composed of fibrous sheets (impregnated with a phenol-formaldehyde resin) with an alkyd resin, electrical arc-resistant materials are obtained.<sup>45</sup>

Safford<sup>46</sup> made insulated electrical coils by extruding a definite thickness of flexible alkyd resin on an electrical conductor, curing the resin, extruding a second layer on the cured coat, winding the conductor so insulated into a coil, pressing the wound coil in a mold and curing the product with heat.

An electrical insulating material may be made from a mixture of a water-insoluble cellulose ether and methylene diaralkyl or diaryl ethers (methylene dibenzyl or diphenyl ethers and their lower alkyl or alkoxy derivatives) and alkyd resins.<sup>47</sup>

A composition proposed by Groten<sup>48</sup> for molded insulation consists of asphalt (gilsonite) and portland cement mixed with an oil-modified alkyd resin dispersed in linseed oil containing copal.

Hovey<sup>49</sup> has used an alkyd resin solution as a temporary binder for inorganic insulating compositions to permit the bending of wire without cracking the insulation. A copper wire is first given a coating of oxide or lead borate followed by a thin coat of alkyd resin. A coil is wound and the resin volatilized by heating 2 hours at 380–400°C. and a final insulation is then applied consisting of mixtures of water glass, asbestos, flint or magnesium oxychloride and other hydraulic cements.

#### ABRASIVES

Resins of the alkyd type, because of their resistance to water, can be utilized as binding agents for abrasants, e.g., alumina, emery and Carborundum.<sup>51</sup> Similar applications are mentioned by Barringer<sup>52</sup> who formed grinding wheels, whetstones, sandpaper and other articles by bonding abrasive grains with the condensation product of a polybasic acid and a polyhydric alcohol. The resin may be powdered, or dissolved in a solvent, before admixture with the abrasive. Plasticizing agents, e.g., indene polymer, tricresyl phosphate, glycol diacetate, triacetin, cumarone resin or pitch, may be added, and the material is molded at 150°C. after

British P. 370,323, 1930, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 3018. See also British P. 390,322, 1929, to International General Electric Co.; *Chem. Abs.*, 1933, 27, 5847.

<sup>43</sup> *Rubber Age*, 1933, 33, 108. See Chapter 69 for the electrical properties of alkyd resins.

<sup>44</sup> E. C. Pitman, U. S. P. 2,000,095, May 7, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 4104.

<sup>45</sup> L. E. Barringer, U. S. P. 1,915,989, June 27, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 4605. British P. 387,066, 1931, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 5446.

<sup>46</sup> M. M. Safford, U. S. P. 1,975,750, Oct. 2, 1934, to General Electric Co.; *Chem. Abs.*, 1934, 28, 7384. See also G. F. Hadley, U. S. P. 1,915,311, Feb. 27, 1933, to Westinghouse Elec. & Mfg. Co.; *Brit. Chem. Abs.*, B, 1934, 307.

<sup>47</sup> D. Traill, British P. 399,308, 1933, to Imperial Chem. Ind. Ltd.; *Chem. Abs.*, 1934, 28, 1795.

<sup>48</sup> F. J. Groten, British P. 397,405, 1933, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.*, B, 1933, 390.

<sup>49</sup> A. G. Hovey, British P. 390,436, 1932, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 5125.

<sup>51</sup> British P. 376,121, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, B, 1932, 902. French P. 724,726, 1931; *Chem. Abs.*, 1932, 26, 4930. French P. 756,907, 1933, to Minnesota Mining & Mfg. Co.; *Chem. Abs.*, 1934, 28, 2490.

<sup>52</sup> L. E. Barringer, U. S. P. 1,908,151, Nov. 6, 1934, to General Electric Co. British P. 381,711, 1932, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 3759. See also R. S. Daniels, British P. 347,677, 1928, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 2880.

which it is cured by heating without pressure. Alternatively, powdered abrasive material may be applied to cloth or paper coated with a solution of the resin and a plasticizing agent and the resin hardened by heat. Robie<sup>55</sup> used glycerol-phthalic anhydride resin, incorporated with inorganic or organic fillers, as a binder. Novotny<sup>56</sup> prepared an abradant by heating abrasive grains, gum accroides, a phenolic substance, a hardening agent, aldehydes and an alkyd resin.

#### MISCELLANEOUS APPLICATIONS

Alkyd resins are employed in the production of a friction material for brake linings.<sup>55</sup> Layers of asbestos cloth and brass wire are coated with a solution of the phthalic anhydride-glycerol condensation product which may be modified with oleic acid. After drying, the layers are heated and molded under pressure.

Dissolved in a volatile solvent, alkyd resins have been employed to cement sand in preparing a foundry-core composition, which can be hardened by baking. These resins are volatilizable at the temperature of the molten metals used for casting.<sup>56</sup>

Alkyd resins have also been utilized as binders in the manufacture of a hard metal composition (cobalt-tungsten carbide).<sup>57</sup> The method is carried out as follows: A mixture of tungsten with 3-10 per cent of carbon and not more than 25 per cent of cobalt is ground, moistened with acetone and mixed into a stiff paste with 2 per cent of a glycerol-phthalic anhydride resin. The paste is shaped, dried and sintered under pressure at 1375°C. Alternatively, a mixture of 80-97 per cent of tungsten carbide and from 3-20 per cent of cobalt in powder form may be pressed into bars which are sintered at 1375°C.

Rohlf<sup>58</sup> utilized alkyd resins, in the intermediate B stage, for cementing layers of cloth or paper. The alkyd-coated layers are subjected to a pressure of 1000 pounds per square inch at the softening-temperature of the resin, 125-140°C. These conditions are maintained for 14-16 hours to cure the binder without changing the character of the sheet material. A fibrous composition product, applicable as transformer spools, refrigerator trays or door strips, has been made by impregnating layers of interlocked fibers of wet paper pulp with a binder of alkyd resin, drying the mass and molding it under heat and pressure.<sup>59</sup> Dyes, pigments and fillers (e.g., clay, asbestos, mica, talc, silica) may be added. Groff<sup>60</sup> developed a process for making laminated sheets in which paper, cardboard or fabric is impregnated with a solution of an alkyd resin, dried and heated at 110-150°C. until the resin is converted to a tough infusible modification, resistant to water and all ordinary solvents. The sheets are coated by dipping or spraying with a reactive varnish of the phenol-aldehyde type and dried to expel the solvent. The coated sheets are then superposed and consolidated by heat and pressure. Products manufactured in this way are characterized by high shock-resistance and can be used for making silent gearing, piston segments and clutch linings.

<sup>55</sup> N. P. Robie, British P. 333,409, 1929, to Carborundum Co., Ltd.; *Brit. Chem. Abs.* B, 1930, 990.

<sup>56</sup> E. E. Novotny, U. S. P. 1,907,088, May 2, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3877.

<sup>57</sup> H. W. H. Warren and R. Newbound, British P. 300,309, 1927, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 23, 4031.

<sup>58</sup> R. Earl, U. S. P. 1,831,555, Nov. 10, 1931, to General Electric Co.; *Chem. Abs.*, 1932, 26, 685. British P. 362,090, 1930, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.* B, 1932, 366.

<sup>59</sup> S. L. Hoyt, U. S. P. 1,794,229 and F. C. Kelley, U. S. P. 1,794,300, Feb. 24, 1931, both to General Electric Co.; *Brit. Chem. Abs.* B, 1931, 932.

<sup>60</sup> H. C. Rohlf, U. S. P. 1,846,373, July 5, 1932, to General Electric Co.; *Chem. Abs.*, 1932, 26, 4428. British P. 305,671, 1928, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 23, 4785.

<sup>61</sup> R. H. Kienle and W. J. Scheiber, British P. 393,412, 1933, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 5910.

<sup>62</sup> F. Groff, U. S. P. 1,673,239, June 12, 1928, to Bakelite Corp.; *Chem. Abs.*, 1928, 22, 2819. German P. 543,442, 1923, to Bakelite Corp.; *Chem. Abs.*, 1923, 26, 2561. British P. 300,596, 1928, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 4090. French P. 643,963, 1923, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 2793. See also G. H. Gardner, British P. 413,684, 1934, to Bushing Co., Ltd.; *Chem. Abs.*, 1935, 29, 344.

Wright<sup>61</sup> produced a molding composition from alkyd resin (10 parts), polymerized vinyl chloride (40 parts), dibutyl phthalate (30 parts), alpha cellulose (7.5 parts) and Titanox (12.5 parts). Switch plates can be made by hot-pressing the resin in a mold whose surface is sprinkled with a finely divided metal, e.g., bronze, copper or aluminum powder, to improve the appearance of the final product.<sup>62</sup> Another method, developed by de Bell,<sup>63</sup> consists in treating a filler with an alkyd resin, after which the material is comminuted, mixed with a phenol-aldehyde product and molded. Montan wax, zinc stearate or other lubricants may be added. Watson<sup>64</sup> molded tubes and spools for electrical appliances from kraft sulphite sheet wood pulp impregnated with shellac, phenol-aldehyde or glycerol-phthalic anhydride resins.<sup>65</sup>

Alkyd or phenol-formaldehyde resins, mixed with high-boiling plasticizers, may be formed into "non-breakable" watch glasses, which are hard at ordinary temperatures, but soften at about 200°C.<sup>66</sup> Such resins may be employed also in the manufacture of spinning-nozzles for artificial silk.<sup>67</sup> Dentures are produced by heating the resin to incipient gelation, molding and converting to the infusible state under pressure at 140-200°C. Heating is continued until the articles are practically non-plastic at 36°C.<sup>68</sup>

Composition tiles for use in refrigerators and in building construction may be formed from asbestos and an inorganic binder, together with a water-impervious, heat-resisting coating of one or more alkyd resins, capable of becoming infusible and insoluble on heating, a plasticizer and an opaque filler.<sup>69</sup> A fire-resisting panel comprised of layers of asbestos with a wood veneer may be constructed by impregnating the layers with an alkyd resin and uniting them under heat and pressure.<sup>70</sup>

Sherburne<sup>71</sup> has described a method of making phonograph needles by impregnating styli of bamboo with a hardened alkyd resin or a mixture of the resin with a drying oil. The glycerol-phthalic anhydride resin has been applied in making sound records.<sup>72</sup> A thin metal disc or metal gauze is coated on one or both sides with the alkyd resin, and an additional thin coating of shellac is applied for receiving the sound-groove impressions. A transparent, flexible, condensation product of a polyhydric alcohol and a polybasic acid is proposed as a base in the making of photographic film.<sup>73</sup> A filler consisting of metal powder, obtained by thermal decomposition of metal carbonyls, has also been used with alkyd resins.<sup>74</sup>

<sup>61</sup> J. G. E. Wright, British P. 387,928, 1933, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 5996.

<sup>62</sup> J. Eaton, British P. 301,432, 1927, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 23, 4090.

<sup>63</sup> J. M. de Bell, British P. 345,489, 1929, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1932, 26, 2073. See also R. H. Kienle and P. F. Schlingman, British P. 421,866, 1934, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1935, 240.

<sup>64</sup> H. L. Watson, British P. 284,232, 1927, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1928, 22, 4679.

<sup>65</sup> See also French P. 38,004, 1930, addn. to 660,347, 1929, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1932, 26, 267; *Chem. Abs.*, 1930, 24, 1738.

<sup>66</sup> H. E. Lindhe, British P. 371,451, 1931, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 3630. French P. 709,908, 1931, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 1080.

<sup>67</sup> Germain P. 530,660, 1928, to Bakelite G.m.b.H.; *Chem. Abs.*, 1932, 26, 1121.

<sup>68</sup> J. H. Schmidt, Canadian P. 309,680, 1931, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 3136. British P. 346,661, 1930; *Chem. Abs.*, 1933, 27, 455. See also I. J. Dresch, U. S. P. 1,862,336, June 7, 1932, to Prosthetic Products, Inc.; *Chem. Abs.*, 1932, 26, 4145.

<sup>69</sup> L. E. Barringer, U. S. P. 1,781,267, July 16, 1929, to General Electric Co.; *Chem. Abs.*, 1929, 23, 4321. L. E. Barringer, Canadian P. 280,906, 1928, to Canadian General Electric Co., Ltd.; *Chem. Abs.*, 1929, 23, 3061. French P. 648,424, 1927, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1929, 23, 2310.

<sup>70</sup> G. H. Gardner, British P. 413,727, 1934, to the Bushing Co., Ltd.; *Chem. Abs.*, 1930, 23, 581.

<sup>71</sup> A. J. Sherburne, British P. 308,370, 1923, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1930, 24, 213.

<sup>72</sup> H. N. Sporborg, A. P. Young and A. T. Ward, British P. 299,752, 1927, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1929, 23, 3548.

<sup>73</sup> O. Schmidt, U. S. P. 1,929,390, Oct. 3, 1933, to General Electric Co.; *Chem. Abs.*, 1934, 28, 58.

<sup>74</sup> British P. 418,006, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1541.

Parchment-like paper may be produced by impregnating (at 140-160°C. for 1-3 minutes) unsized paper with a molten, partly polymerized alkyd resin plasticized with tricresyl phosphate.<sup>76</sup> More complete polymerization is effected by heating for 6 hours at 130°C.

Safford<sup>76</sup> prepared printing and offset rolls by extruding a mixture of cured and uncured alkyd resins, together with a filler (cork, titanium oxide) onto a core and curing the resinous layer by heat.

Synthetic resins from polyhydric alcohols and aliphatic or aromatic dicarboxylic acids have been employed in the manufacture of artificial threads. The resins, together with a softening agent, are dissolved in an organic solvent, e.g., cyclohexanone, and spun into a precipitating-bath containing acetic acid, sodium perchlorate or sodium thiocyanate.<sup>77</sup> The swollen threads are stretched in several increasing steps and then shrunk before collecting on a receiving device.

A metallic mirror for withstanding high temperatures consists of a silver reflecting surface, a coating of copper on the silver, and a backing of an aluminum alloy. The alloy is attached to the copper surface by a cement containing an alkyd resin.<sup>78</sup> A self-lubricating metallic body can be obtained by cementing a paste of graphite onto a metallic surface with an adhesive containing a polyhydric alcohol-polybasic acid resin.<sup>79</sup>

Barringer and Rohlf<sup>80</sup> suggest the following procedure for making laminated glass. A layer of alkyd resin is placed between the glass sheets and a pressure of the order of 50 pounds per square inch is applied at 110°C. for 5 minutes, after which the temperature is lowered to 70-75°C. while the pressure is gradually increased to 200 lbs. The cooling is completed under pressure.

Sheets of cellulose ester and glass can be cemented by the condensation product of a polyhydric alcohol, a polybasic acid and a glycerol ester of a fatty acid.<sup>81</sup> Macht<sup>82</sup> added pyroxylin and a pyroxylin plasticizer to an alkyd resin to form an adhesive for this purpose. Laminated sheets of cellulose esters, used for wrappings or similar purposes, have been made with an alkyd resin as the adhesive for uniting the sheets.<sup>83</sup> In the production of sheet material from urea-aldehyde resins, the incorporation of an alkyd resin is said to increase the stability of the final product.<sup>84</sup>

Hovey<sup>85</sup> mixed from one to two parts of nitrocellulose with a resin made from phthalic anhydride, glycerol, linseed oil fatty acids, ethylene glycol, tung oil and rosin to make a cementing composition.

Alkyd resins are also used in the preparation of a softener for cellulose ester adhesives, e.g., pyroxylin or cellulose acetate cements, used to unite shoe parts.<sup>86</sup> The softener is made by heating diethylene glycol, phthalic anhydride and tung oil under a reflux condenser with agitation.

<sup>76</sup> F. O. Reiss, British P. 397,550, 1932, to Aladdin Industries, Ltd.; *Brit. Chem. Abs. B*, 1933, 960.

<sup>77</sup> M. M. Safford, British P. 403,905, 1934, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1934, 28, 3852.

<sup>78</sup> British P. 387,976, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 301.

<sup>79</sup> I. S. Crocker, U. S. P. 1,953,796, April 3, 1934, to General Electric Co.; *Chem. Abs.*, 1934, 28, 3852.

<sup>80</sup> British P. 415,116, 1934, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1935, 29, 857.

<sup>81</sup> L. E. Barringer and H. C. Rohlf, British P. 367,523, 1930, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 3052.

<sup>82</sup> J. C. Zola, U. S. P. 1,908,004, May 9, 1933, to Duplate Corp.; *Chem. Abs.*, 1933, 27, 3794. U. S. P. 1,920,619, Aug. 1, 1933; *Chem. Abs.*, 1933, 27, 4896.

<sup>83</sup> M. L. Macht, U. S. P. 1,906,474, Feb. 5, 1933, to Duplate Corp.; *Brit. Chem. Abs. B*, 1934, 196.

<sup>84</sup> J. E. Snyder, U. S. P. 1,992,249, Feb. 26, 1935, to Du Pont Cellophane Co.; *Chem. Abs.*, 1935, 29, 2627.

<sup>85</sup> T. H. Müller, British P. 419,306, 1933; *Brit. Chem. Abs. B*, 1935, 69. For a discussion of the stability of urea resins see Chapter 27.

<sup>86</sup> A. G. Hovey, U. S. P. 1,925,903, Sept. 5, 1933, to General Electric Co.; *Chem. Abs.*, 1933, 27, 5493. British P. 386,335, 1931, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1933, 238. French P. 42,244, 1933, addn. to 726,745, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 27, 4891. Allgemeine Elektrizitäts-Ges., British P. 390,322, 1926, to International General Electric Co.; *Chem. Abs.*, 1933, 27, 5847. See Chapter 47.

<sup>87</sup> W. H. Wedge, British P. 399,525, 1933, to Boston Blacking Co., Ltd.; *Chem. Abs.*, 1934, 28, 1824.

## Chapter 50

### Miscellaneous Resins Containing Oxygen Linkages

Polyethylene oxides and polyvinyl ethers, described in this chapter, are compounds which structurally resemble cellulose in that they are long, linear molecules (see Chapter 4). Their development as synthetic resins is a recent one, and parallel with technical progress there has been an advance in the elucidation of the constitution of this group of compounds, particularly by Staudinger and his co-workers. The inclusion of polyanhydrides, lactic acid, shellac and carbon suboxide is justified by similarities in the structure of the resinous bodies derived from them.

#### POLYETHYLENE OXIDE AND RELATED COMPOUNDS

Ethylene oxide,  $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} \text{O}$ , is a liquid boiling at 12.5°C., and characterized by

a very strong tendency to polymerize. It was prepared by Wurtz<sup>1</sup> from ethylene chlorohydrin and caustic potash, and is obtained also directly from silver oxide and ethylene dibromide at 250°C., a method which elucidates the formula of the compound.<sup>2</sup> When heated with water in a closed tube ethylene oxide forms glycol and polyethylene glycols.<sup>3</sup> Staudinger and Schweitzer<sup>4</sup> separated a series of fractions from such a mixture which varied from glycol,  $\text{HOCH}_2\text{CH}_2\text{OH}$ , a heavy liquid boiling at 180°C. to the sixfold polymer,  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_6\text{H}$ , a very viscous liquid boiling at 325°C. at a pressure of 0.025 mm. Wurtz<sup>2</sup> also obtained a series of polyethylene acetates from the corresponding glycols, but neither the glycols nor the acetates could be isolated in a pure state.

Later, Wurtz<sup>5</sup> observed the formation of a solid ethylene oxide on allowing the monomeric compound to stand in contact with a trace of alkali or zinc chloride. This polymerized oxide melted at 56°C. and was soluble in water and alcohol but insoluble in ether. Roithner<sup>7</sup> noted that reaction took place more rapidly at 50-60°C. in the presence of alkali.

Staudinger and Schweitzer<sup>8</sup> found that polymerization of ethylene oxide with anhydrous stannic chloride occurred readily at -80°C. This agent has a well-established polymerizing action on unsaturated hydrocarbons such as styrene, indene, isoprene, or cyclopentadiene.<sup>9</sup> Metallic sodium or potassium and trimethylamine also were effective catalysts. Reaction with stannic chloride was carried out at low temperatures, as the heat of polymerization (20 to 30 calories per mol) was liberated so rapidly at room temperature that unpolymerized oxide was

<sup>1</sup> A. Wurtz, *Ann.*, 1869, 110, 125; *Ann. chim. phys.*, 1863, 69 (3), 317.

<sup>2</sup> Greene, *Jahresberichte*, 1877, 552. Methods for preparing ethylene oxide are reviewed by Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1934.

<sup>3</sup> A. Wurtz, *Ann. chim. phys.*, 1863, 69, 330. M. A. von Lourenço (*Ann. chim. phys.*, 1863, 67, 274) also prepared polyethylene glycols by heating a mixture of ethylene glycol and ethylene bromide.

<sup>4</sup> H. Staudinger and O. Schweitzer, *Ber.*, 1929, 62, 2395.

<sup>5</sup> A. Wurtz, *Ann. chim. phys.*, 1863, 69, 334.

<sup>6</sup> A. Wurtz, *Ber.*, 1879, 10, 90; *Bull. soc. chim.*, 1878, 29 (2), 530.

<sup>7</sup> E. Roithner, *Monatsh.*, 1894, 15, 679; *J.C.S.*, 1895, 68 (1), 319.

<sup>8</sup> H. Staudinger and O. Schweitzer, *loc. cit.*

<sup>9</sup> H. Staudinger and H. A. Bruson, *Ann.*, 1926, 447, 110.

suddenly volatilized with the development of extremely high pressures, often resulting in explosions. The product with stannic chloride was divided into a series of fractions by solution in benzene and fractional precipitation with ether. The average molecular weight of the initial material was 3000, and this yielded five fractions ranging in molecular weights from 4650-4900 to 430,440.<sup>10</sup> The melting points and viscosities were lower, and the solubilities in ether higher, for the lower polymers. (See Figure 130.)

The effect of various catalysts on the polymerization of ethylene oxide at 20°C. is given in Table 49.<sup>11</sup>

TABLE 49.—Rate of Polymerization of Ethylene Oxide with Various Catalysts.

Catalyst	Yield of Polymer	Molecular Weight	Time
Trimethylamine, Sodium, Potassium, Stannic chloride } .. . . .	5%	2,000	1-2 weeks
Sodamide. ....	1- 2%	10,000	2-3 months
Zinc oxide .....	10-20%	60,000	3-4 months
Strontium oxide .....	10-20%	100,000	2-3 months
Calcium oxide. ....	50%	120,000	about 2 years

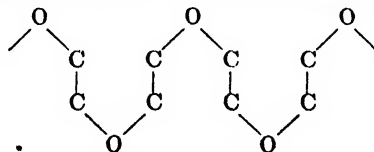
Oxides of iron, magnesium, or lead, silica gel, and activated carbon did not effect polymerization. Aluminum oxide very slowly yielded hemicolloids. Melting points and viscosities increased with the degree of polymerization. Hard products were obtained only when the viscosity was high, such materials possessing the property of yielding tough films. All the polyethylene oxides were shown by x-ray diagrams to be crystalline and viscosity measurements indicated a meandering structure for the molecule.<sup>12</sup>

Propylene oxide also polymerizes with vigor under the influence of stannic chloride. Low (liquid) polymers constitute the main product, but semi-solid polymers may be obtained by fractionation. The latter have a molecular weight of approximately 9000 and are soluble in benzene, whereas polyethylene oxide of the same degree of polymerization is only slightly soluble in benzene and melts at about 60°C.<sup>13</sup> On heating propylene oxide at 117°C. with potassium hydroxide for 12 days a triether,  $C_6H_{12}O_4$  (b.p. 128-130°C. at 2.4 mm.), and a tetramolecular condensation product,  $C_{12}H_{20}O_6$  (b.p. 120-140°C. at 2.4 mm.), are obtained.<sup>14</sup>  $\gamma$ -Phenyl- $\beta$ -benzylpropane- $\beta$ -diol treated with concentrated sulphuric acid at 0°C. yields resinous products only, but on boiling with 20 per cent sulphuric acid or anhydrous oxalic acid,  $\gamma$ -phenyl- $\beta$ -benzyl- $\alpha,\beta$ -propylene oxide (m.p. 78°C.) is formed.<sup>15</sup> The latter proved to be a stable compound which did not isomerize,

<sup>10</sup> R. Signer and H. Gross (*Helv. Chim. Acta*, 1934, 17, 335; *Chem. Abs.*, 1934, 28, 4287) report the molecular weight of polyethylene oxide in ethylene bromide, determined by ultracentrifugal methods, as 70,000.

<sup>11</sup> H. Staudinger and H. Lohmann, *Ann.*, 1933, 505, 41.

<sup>12</sup> The meandering structure of polyethylene oxide may be represented by



See Chapter 4. This type of structure was also indicated by x-ray studies made by E. Sauter, *Z. phys. Chem.*, 1933, 21, 161, 186; *Chem. Abs.*, 1933, 27, 3867.

<sup>13</sup> See H. Staudinger, "Hochmolekulare Organischen Verbindungen," Verlag Julius Springer, Berlin; 1932, 298.

<sup>14</sup> P. A. Levene and A. Walti, *J. Biol. Chem.*, 1927, 75, 325; *Brit. Chem. Abs. A*, 1927, 1166.

<sup>15</sup> M. Tiffeneau, A. Orékhov and J. Lévy, *Bull. soc. chim.*, 1931, 49 (4), 1840; *Brit. Chem. Abs. A*, 1932, 395.

suggesting that substitution destroys the tendency towards polymerization in this series of oxides.

#### DERIVATIVES OF POLYETHYLENE OXIDE

Polyethylene oxides yield a number of derivatives which differ but little in their physical properties from the corresponding polymerized oxide. Staudinger considers that polyethylene oxide is a dihydrate with the formula  $\text{HOCH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_x-\text{CH}_2\text{CH}_2\text{OH}$ . One explanation for the formation of the long chain is as follows: a molecule of ethylene oxide takes up a molecule of water to give glycol, which then reacts with another molecule of the oxide to give a polyglycol. The latter in turn combines with still another molecule of the oxide, thus building up the chain. Acetylation of the polymer transforms it into a diacetate to which is assigned the formula,  $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{CH}_2\text{O})_x-\text{CH}_2\text{CH}_2\text{OOCCH}_3$ . The action of other reagents on the end-groups offers the possibility of introducing various elements into the molecule. Staudinger has used, for example, tri- and

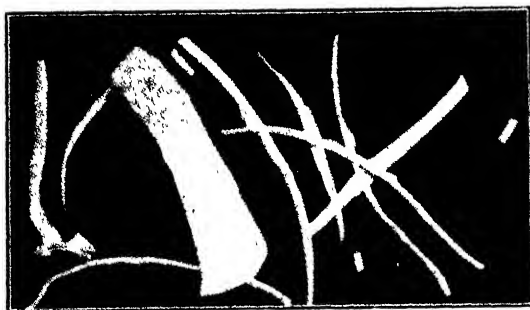


FIG. 130.—Polyethylene Oxide Eucolloid Prepared by H. Staudinger. Molecular Weight About 70,000.

dimethylamine as catalysts in bringing about polymerization, and the resulting material actually contained combined nitrogen.<sup>16</sup> In this instance the initial product was possibly an ethanolamine,  $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ , to which another molecule of oxide could add giving the ether,  $\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ . Continuation of such reactions results in long-chain molecules of high molecular weights. Similar explanations are offered by Hibbert and Perry,<sup>17</sup> who also report that polymerization of ethylene oxide in methyl alcohol as a solvent furnishes compounds having methoxy terminal groups.

From ethylene chlorohydrin and ethylene oxide in the molecular ratio 1:10, a polymer containing chlorine was obtained. This consisted mainly of polyethylene oxide chlorohydrate. By fractional precipitation two solid polymers were separated with degrees of polymerization of approximately 23 and 100 (i.e., 23 and 100 monomeric groups per molecule).<sup>18</sup>

Polymerization of alkylene oxides is carried out commercially by passing the

<sup>16</sup> H. Staudinger, "Hochmolekularen Organischen Verbindungen," Verlag Julius Springer, Berlin, 1932, 257 et seq.

<sup>17</sup> H. Hibbert and S. Z. Perry, *Can. J. Research*, 1933, 8, 102; *Brit. Chem. Abs. A*, 1933, 373. A hypothesis of the formation of sugars and polysaccharides in plants based on the theory of the polymerization of ethylene oxide is given by H. Hibbert, *Can. J. Research*, 1933, 8, 103; *Chem. Abs.*, 1933, 27, 1866.

<sup>18</sup> H. Staudinger, "Hochmolekularen Organischen Verbindungen," Julius Springer, Berlin, 1932, 300. See also, A. Wirth, *Ann.*, 1863, 69, 331.



vapor at 40-60°C. over alkaline catalysts, such as caustic potash or caustic soda.<sup>19</sup> The degree of polymerization may be increased by employing higher temperatures, e.g., 120°C.<sup>20</sup> Ethylene oxide, for example, conducted over caustic soda forms a waxy mass. When anhydrous sodium bisulphate is used, dioxane is the chief product. Other procedures involve dissolving the oxide in an inert solvent,<sup>21</sup> e.g., carbon tetrachloride, benzene, or ethyl acetate, or in polyethylene glycol containing the alkaline catalyst,<sup>22</sup> and heating under pressure.

These viscous or solid polymers are employed as dispersing agents: a dispersion of montan wax with carnauba wax and castor oil may serve for floor polish and a dispersion with green earth (a ferrous silicate) and fuchsin is added to lime paints.<sup>23</sup> Other uses are as fillers for wood, as pastes, or for solutions or emulsions with which waxes, resin, or cellulose derivatives may be incorporated.<sup>24</sup> The polymers also find application in the manufacture of plastic molding compositions in which they serve as softeners,<sup>25</sup> in the preparation of colored pigments and lakes,<sup>26</sup> and as assistants in dyeing or stripping of dyes from textile fabrics.<sup>27</sup>

An agent for removing paint, varnish, and other coatings by pickling is made from a wax-like polymerization product (m.p. 50°C.) of ethylene oxide, xylene, butyl acetate, dichloroethylene and benzene.<sup>28</sup> The elasticity of such materials as collodion, wool, benzylcellulose, celluloid, leather, phenol-aldehyde condensation products or wood is increased by inclusion of alkylene oxide polymers.<sup>29</sup> Solutions of ethylene oxide polymer and collodion cotton or benzylcellulose in a mixture of benzene, toluene, butyl acetate and ethyl alcohol have been recommended as lacquers.<sup>30</sup> Waxes to be used as polishing compositions are obtained by the treatment of ethylene, propylene, or trimethylene oxide with natural or synthetic waxes or with paraffin, the materials being heated together at 120°-180°C. for several hours.<sup>31</sup>

By treating albumin with ethylene oxide, or other alkylene oxides, syrupy hygroscopic substances are formed which are soluble in water and are precipitated therefrom by tannin and picric acid. These condensation products are therapeutic agents.<sup>32</sup> Shellac and ethylene oxide, at 150°C., form resinous products which may be used in varnishes.<sup>33</sup> For example, 300 parts of shellac (acid value of 55) are treated with 90 parts of the oxide to give 350 parts of a viscous, dark colored resin. Similarly, colophony, ester gum or resins from phthalic anhydride and glycerol may be combined with ethylene oxide.

Esterification or etherization of non-carbohydrate organic compounds (containing hydroxyl or carboxyl groups) with polyethylene glycols or their monoethers or esters having at least four (C<sub>2</sub>H<sub>4</sub>O) groups yields wetting, foaming, or cleansing

<sup>19</sup> F. Webel, U. S. P. 1,921,378, Aug. 8, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5082. M. Wittmer, U. S. P. 1,976,078, Oct. 9, 1934; *Chem. Abs.*, 1934, 28, 7261. British P. 346,550, 1930; *Brit. Chem. Abs. B*, 1931, 666.

<sup>20</sup> F. Webel, German P. 597,496, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5080.

<sup>21</sup> French P. 750,520, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 782.

<sup>22</sup> British P. 406,443, 1932, addn. to 346,550, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1934, 1393.

<sup>23</sup> British P. 353,926, 1930; *Brit. Chem. Abs. B*, 1931, 1132; French P. 706,105, 1930; *Chem. Abs.*, 1932, 26, 223; both to I. G. Farbenind. A.-G. L. Kollek and F. Pohl, U. S. P. 1,930,853, Oct. 17, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 236.

<sup>24</sup> British P. 349,638, 1930; *Chem. Abs.*, 1932, 26, 2070. German P. 529,494, 1930; *Chem. Abs.*, 1931, 25, 5048. French P. 705,852, 1930; *Chem. Abs.*, 1932, 26, 268. All to I. G. Farbenind. A.-G.

<sup>25</sup> British P. 352,042, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3391.

<sup>26</sup> French P. 717,414, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2878.

<sup>27</sup> British P. 367,420, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2044.

<sup>28</sup> L. Kollek, German P. 542,770, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3393.

<sup>29</sup> L. Kollek and W. Engels, U. S. P. 1,942,146, Jan. 2, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1961. German P. 560,703, 1930; *Chem. Abs.*, 1933, 27, 1114.

<sup>30</sup> L. Kollek, U. S. P. 1,937,114, Jan. 8, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1068.

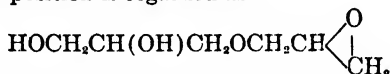
<sup>31</sup> British P. 346,438, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 614.

<sup>32</sup> H. Weyland, U. S. P. 1,596,785, Aug. 17, 1926; *Chem. Abs.*, 1926, 20, 3332.

<sup>33</sup> O. Schmidt and E. Meyer, U. S. P. 1,845,103, Feb. 16, 1932; *Chem. Abs.*, 1932, 26, 2334.

agents.<sup>34</sup> Alcohols containing between 8 and 18 carbon atoms, particularly those from the catalytic reduction of vegetable oils and fats, fatty acids, or the hydrolysis of sperm oil, are especially applicable as the non-carbohydrate material. According to Oda,<sup>35</sup> ethylene glycol reacts with vegetable oils to furnish bodies which are soluble in ethyl alcohol. Distillation of the product from glycol and olive oil at 200°C. gives a residue which can be sulphonated to an emulsifying agent. A drying oil is obtained from glycol and linseed oil.

Glycidol,  $\text{O} \begin{array}{c} \text{CHCH}_2\text{OH} \\ | \\ \text{CH}_2 \end{array}$  heated for 42 hours at 100°C., yields a condensation product whose composition is regarded as<sup>36</sup>



At higher temperatures, substances having the same empirical formula but greater molecular weights are obtained. Polyglycidols may be prepared by polymerization of glycidol at low temperatures with the aid of condensing agents,<sup>37</sup> e.g., by treatment with stannic chloride at -25°C. Solid calcium chloride caused the rapid polymerization of glycidol (prepared from glycerol monochlorohydrin) to a water-soluble red tar. The reaction was highly exothermic.<sup>38</sup> Distillation of glycidol acetate, which had stood for 5 days at 135-140°C. or for several weeks at 12-13°C., gave the dimeric glycidol acetate (which slowly polymerized further), incompletely acetylated glycerols, monoacetin, triacetin, and polymers of glycidol acetate.<sup>39</sup>

#### POLYGLYCEROLS

In the distillation of crude glycerol, residues or foots are obtained which contain not only glycerol but also polymerized glycerol, aldehyde resins and other decomposition products together with salts. It has been stated that the residues can be dissolved in water, acidified, treated with lime, filtered, evaporated and redistilled in order to recover some of the glycerol.<sup>40</sup>

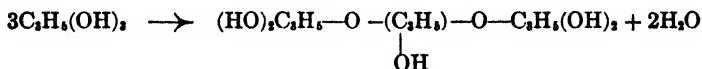
The dehydration of glycerol may be considered to take place either intermolecularly or intramolecularly. The first reaction, in which the elimination of water takes place between molecules, yields an ether type of linkage



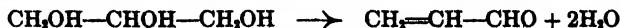
When one molecule of water is eliminated (i.e.,  $y=1$ ) diglycerols are formed



When two molecules of water are lost between three molecules of glycerol, triglycerols result



In the presence of iron, or iron salts, intramolecular loss of water occurs with the formation of acrolein.<sup>41</sup>



<sup>34</sup> British P. 380,431, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1932, 1114.

<sup>35</sup> R. Oda, *J. Soc. Chem. Ind. Japan*, 1932, 35, 515B; *Chem. Abs.*, 1933, 27, 1222.

<sup>36</sup> P. A. Levene and A. Walti, *J. Biol. Chem.*, 1927, 75, 325; *Brit. Chem. Abs.* A, 1927, 1166.

<sup>37</sup> G. Frank, German P. 575,750, 1933; *Chem. Abs.*, 1934, 26, 1720.

<sup>38</sup> T. H. Rider and A. J. Hill, *J.A.C.S.*, 1930, 52, 1521.

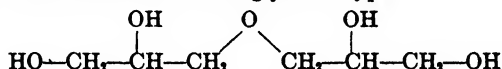
<sup>39</sup> P. A. Levene and A. Walti, *J. Biol. Chem.*, 1928, 79, 263; *Chem. Abs.*, 1929, 23, 99.

<sup>40</sup> E. Lewis, *J.S.C.I.*, 1922, 41, 97T. See J. W. Lawrie, "Glycerol and the Glycols," Chemical Catalog Co., New York, 1928.

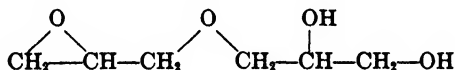
<sup>41</sup> See Chapter 23.

Von Lourenço<sup>44</sup> prepared diglycerol by heating glycerol under reflux in the presence of hydrogen chloride for 12-15 hours at 100°C. The compound had a boiling point of 220-230°C. at 22 mm.<sup>45</sup> Triglycerol was also obtained under these conditions. Hibbert<sup>46</sup> used 0.05 per cent of iodine as a catalyst and heated the glycerol to 210°C. for 2 hours. On distillation there resulted an 85 per cent yield of water-white, viscous, hygroscopic liquid having a boiling point at 30 mm. of 257-260°C. The diglycerol was soluble in water but insoluble in ether. Moreover glycerol can be heated alone to temperatures of 200-275°C. to yield polyglycerols, especially if an inert gas is led through the solution to eliminate water as quickly as it is formed.<sup>47</sup> According to Lewis,<sup>48</sup> diglycerol occurs to the extent of about 2 per cent in ordinary glycerol and larger amounts are present in the glycerol which is prepared under high pressure in autoclaves.

Rayner<sup>49</sup> concluded that the conversion of glycerol into distillable polymerization products gives rise to substances of 2 types; the first consists of products obtained by intermolecular condensation of the diglycerol type



whereas the second is of the glycidic type in which intramolecular condensation occurs



By assuming the presence of these two types of derivatives the discrepant results of the properties of distillable polymerization products made by various investigators can be explained. By heating glycerol for 12 hours at 270-280°C. and separating the fraction boiling at 210-250°C. at 3 mm., a product is obtained which has a hydroxyl value of 34 per cent and a viscosity 5 times that of glycerol. Similar heating for a longer time and distillation of a fraction boiling at 260-265° at 10 mm. yielded a derivative which had a hydroxyl value of 38 per cent and a viscosity 13 times that of glycerol. From these results it appears that the first distillate contained glycidic, which possess a low viscosity.

The action of fused sodium acetate on 95 per cent glycerol followed by treatment with acetic anhydride and fractionation gives rise to the following derivatives: diglycerol tetra-acetate, triglycerol penta-acetate, tetraglycerol hexa-acetate, pentaglycerol hepta-acetate, hexaglycerol octa-acetate and heptaglycerol nona-acetate.<sup>48</sup> By continuing the condensation a crystalline acetin is obtained which appears to be the same as the diacetin of the homologous diglyceric alcohol from dichlorohydrin which was reported by Fauconnier and Sanson.<sup>49</sup>

Other catalysts include zinc chloride,<sup>50</sup> tantalum, thorium and magnesium oxides<sup>51</sup> together with sodium or potassium silicates as accelerators.<sup>52</sup> Sodium acetate can

<sup>44</sup> M. A. von Lourenço, *Ann. chim. phys.*, 1863 (3), 67, 300. W. Will, *Z. ges. Schliefs- u. Sprengstoffwesen*, 1, 231; *Chem. Zentr.*, 1906, 2, 1000. See also C. Claessen, German P. 181,754, 1906; and 198,768, 1907; *Chem. Zentr.*, 1907, 2, 199; 1908, 2, 120. J. Niviere, *Compt. rend.*, 1913, 156, 1778; *Chem. Abs.*, 1913, 7, 3113.

<sup>45</sup> The diglycerol prepared by J. V. Nef (*Ann.*, 1904, 335, 239) by hydrolysing the glycidic ether boiled at 261-263°C. at 27 mm.

<sup>46</sup> H. Hibbert, U. S. P. 1,126,467, Jan. 26, 1915; *Chem. Abs.*, 1915, 9, 694.

<sup>47</sup> W. Rintoul and A. G. Innes, British P. 24,608, 1910, to Nobel Explosives Co.; *Chem. Abs.*, 1912, 6, 1537.

<sup>48</sup> E. Lewis, *loc. cit.*

<sup>49</sup> A. Rayner, *J.S.C.I.*, 1922, 41, 224T.

<sup>50</sup> M. Rangier, *Compt. rend.*, 1923, 187, 345; *Chem. Abs.*, 1923, 22, 4468.

<sup>51</sup> A. Fauconnier and J. Sanson, *Bull. soc. chim.*, 1887, 48, 236; *J.C.S.*, 1888, 54, 244.

<sup>52</sup> R. I. Bashford, U. S. P. 1,467,399, Sept. 11, 1923, to Grasselli Powder Co.; *Chem. Abs.*, 1923, 17, 3380.

<sup>53</sup> H. Weber and F. Niemeyer, German P. 494,430, 1926, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1930, 24, 2760. British P. 265,146, 1926; *Chem. Abs.*, 1926, 22, 244.

<sup>54</sup> H. Weber and F. Niemeyer, German P. 494,431, 1926 to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1930, 24, 2760. British P. 265,147, 1926; *Chem. Abs.*, 1926, 22, 244.

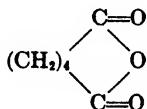
also be used in the presence of inert gases such as carbon dioxide, nitrogen, hydrogen or water gas. Essentially diglycerol is formed under these conditions.<sup>54</sup> The use of mercuric chloride, mercury sulphate, cuprous chloride or ferric chloride in concentrations of 0.1-0.5 per cent with glycerol at temperatures between 250-275°C. yields a highly viscous reaction mixture. If the condensation is carried out in a stream of inert gas, di- and triglycerols are not formed but rather a transparent, brown-yellow colored, viscous liquid which is soluble in water and alcohol and has a flash point above 270°C. The material is said to be useful as a lubricant especially in contact with compressed oxygen inasmuch as it is "explosive-proof."<sup>54</sup>

Ushakov and Obriadina<sup>55</sup> tested the efficacy of various catalysts on the resinification of glycerol and determined that mercurous sulphate, aluminum sulphate and titanium sulphate were effective. Mercurous chloride, mercurous nitrate and mercuric nitrate were ineffective. Maximum yields of resin were obtained by using 4 per cent catalyst and heating for 10-14 hours. Upon vacuum-desiccation a dark brown resin resulted which was soluble in water, alcohol, alcoholic benzene and partially soluble in acetone. Further heating caused the resin to become infusible and insoluble. A baked film was glossy, flexible, insoluble in water and acetone and unaffected by dilute acids and alkalis. If the resin is dissolved in water and steam-distilled, the resulting product is insoluble in hot and cold water but soluble in alcohol and in aqueous alkaline solutions. Later experiments on the polymerization of glycerol indicate that a gelatinous or rubbery product can be prepared.<sup>56</sup>

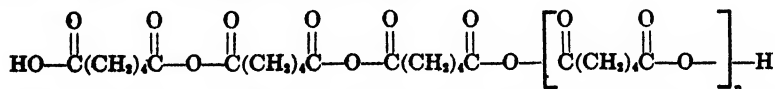
#### POLYANHYDRIDES

Polymerization of the anhydrides of dibasic acids was observed by Hollemann and Voerman.<sup>57</sup> In attempting to measure the rate of reaction of such anhydrides with water, they observed that only those of succinic and glutaric acids gave satisfactory constants. Accurate measurements were not obtained with higher anhydrides (e.g., adipic, pimelic, suberic, azelaic, or sebacic) owing to their sparing solubility in water and polymolecular state. The latter condition was indicated also by boiling point determinations in acetone. Farmer and Kracovsky,<sup>58</sup> however, prepared adipic anhydride from the acid and acetic anhydride and considered it unimolecular.

Later Hill<sup>59</sup> made both a monomeric and a polymeric form of adipic anhydride. The former is a ring compound,



and the latter a linear polymer of the type,



which is broken down by heat *in vacuo*, forming the cyclic monomer. Investigations have been extended also to sebacic  $\alpha$ -anhydride, which is regarded as a chain-

<sup>54</sup> British P. 364,800, 1926, to Henkel & Cie. G.m.b.H.; *Chem. Abs.*, 1928, 22, 244.

<sup>55</sup> K. Noack, German P. 561,193, 1931; *Chem. Abs.*, 1933, 27, 1161. British P. 368,474, 1933; *Chem. Abs.*, 1934, 28, 1356. French P. 735,378, 1932; *Chem. Abs.*, 1933, 27, 1161. See Chapters 23 and 42.

<sup>56</sup> S. N. Ushakov and E. M. Obriadina, *Ind. Eng. Chem.*, 1933, 25, 997. See Chapter 42.

<sup>57</sup> Carleton Ellis, private communication from Ellis-Foster Co.

<sup>58</sup> A. F. Hollemann and G. L. Voerman, *Proc. K. Akad. Wetensch. Amsterdam*, 1903, 6, 410; *J.C.S.*, 1904, 86 (1), 237. For the preparation of adipic anhydride from the acid and acetyl chloride, see Voerman, *Rec. trav. chim.*, 1904, 23, 265.

<sup>59</sup> E. H. Farmer and J. Kracovsky, *J.C.S.*, 1927, 690.

<sup>59</sup> J. W. Hill, *J.A.C.S.*, 1930, 52, 4110.

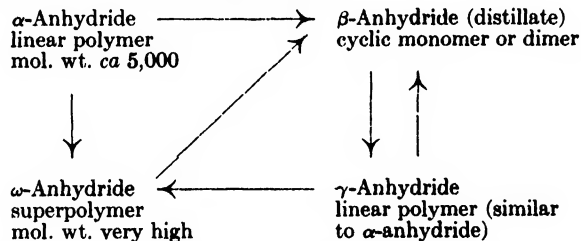
like polymer, formed by the reaction between acetyl chloride or acetic anhydride and sebacic acid.<sup>60</sup> On heating this  $\alpha$ -anhydride to 200°C. in a molecular still<sup>61</sup> it is transformed into a polyanhydride of much higher molecular weight ( $\omega$ -anhydride) and a crystalline distillate ( $\beta$ -anhydride). The latter was shown to be a 22-membered cyclic dimer. At its melting point (68°C.),  $\beta$ -anhydride reverts to a higher polymer,  $\gamma$ -anhydride. At 130°C.  $\omega$ -anhydride is soft enough to be drawn into continuous filaments. These could be cold drawn and the resulting fibers were lustrous and very strong. On standing for a few days, however, they became fragile and brittle.

$\alpha$ -Anhydrides of dibasic acids, containing 7 to 18 carbon atoms, were prepared by the action of acetic anhydride on the corresponding acids.<sup>62</sup> The melting points of the various products are given in Table 50.

TABLE 50.—Melting Points of  $\alpha$ -Anhydrides.

$\alpha$ -Anhydride	Empirical Formula	Melting Point, °C.
Pimelic	$C_7H_{10}O_3$	53-55
Suberic	$C_8H_{12}O_3$	65-66
Azelaic	$C_9H_{14}O_3$	53-53.5
Undecanedioic	$C_{11}H_{18}O_3$	69-70
Dodecanedioic	$C_{12}H_{20}O_3$	86-87
Brassylic	$C_{13}H_{22}O_3$	76-78
Tetradecanedioic	$C_{14}H_{24}O_3$	89-91
Octadecanedioic	$C_{18}H_{32}O_3$	94-95

In all instances  $\alpha$ -anhydrides were linear polymers and when heated in a molecular still yielded  $\omega$ - and  $\beta$ -anhydrides,<sup>63</sup> and the latter in turn, either on further heating or on standing, changed to  $\gamma$ -anhydrides. These transformations can be summarized by the following scheme:



The physical properties of cyclic ( $\beta$ -) anhydrides, obtained by depolymerization of  $\alpha$ -anhydrides, are given in Table 51.

TABLE 51.—Physical Properties of Cyclic Anhydrides.

Acid	Structural Unit of Anhydride	Product of Depolymerization and Size of Ring	Stability	Melting Point °C.
Adipic	$-\text{OC}(\text{CH}_2)_4\text{CO}-\text{O}-$	Monomer 7	Unstable	20
Pimelic	$-\text{OC}(\text{CH}_2)_5\text{CO}-\text{O}-$	Monomer 8	Extremely unstable	Liquid
Suberic	$-\text{OC}(\text{CH}_2)_6\text{CO}-\text{O}-$	Dimer 18	Stable up to m.p.	56-57
Azelaic	$-\text{OC}(\text{CH}_2)_7\text{CO}-\text{O}-$	Monomer 10	Extremely unstable	Liquid
Sebacic	$-\text{OC}(\text{CH}_2)_8\text{CO}-\text{O}-$	Dimer 22	Stable up to m.p.	68
Undecanedioic	$-\text{OC}(\text{CH}_2)_9\text{CO}-\text{O}-$	Monomer 12	Extremely unstable	Liquid
Dodecanedioic	$-\text{OC}(\text{CH}_2)_{10}\text{CO}-\text{O}-$	Dimer 26	Stable up to m.p.	76-78
Brassylic	$-\text{OC}(\text{CH}_2)_{11}\text{CO}-\text{O}-$	Monomer 14	Unstable	Liquid
Tetradecanedioic	$-\text{OC}(\text{CH}_2)_{12}\text{CO}-\text{O}-$	Monomer 15	Unstable	Liquid
Octadecanedioic	$-\text{OC}(\text{CH}_2)_{16}\text{CO}-\text{O}-$	Monomer 19	Unstable	36-37

<sup>60</sup> J. W. Hill and W. H. Carothers, *J.A.C.S.*, 1932, 54, 1569.

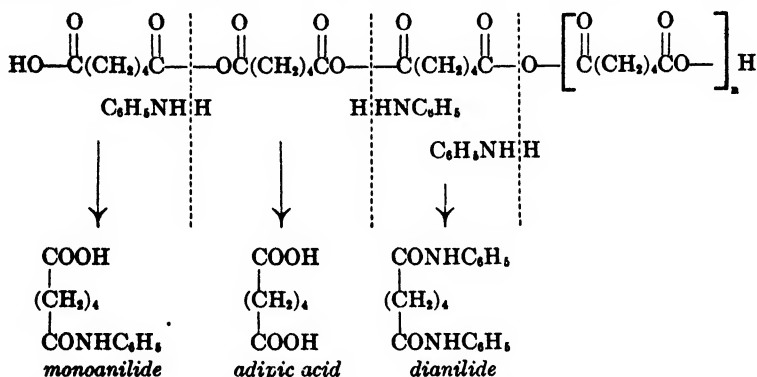
<sup>61</sup> For a description of this still, see, W. H. Carothers and J. W. Hill, *J.A.C.S.*, 1932, 54, 1567.

<sup>62</sup> J. W. Hill and W. H. Carothers, *J.A.C.S.*, 1932, 55, 5022.

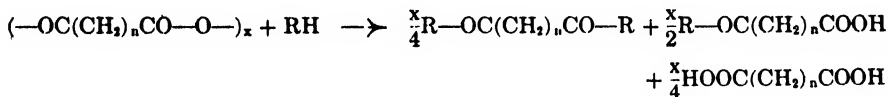
<sup>63</sup> The stereochemistry and mechanism in the formation and stability of large rings is discussed by W. H. Carothers and J. W. Hill, *J.A.C.S.*, 1933, 55, 5043.

It is interesting to note that cyclic anhydrides, particularly those containing 10 or more carbon atoms, possess a spicy or musk-like odor.<sup>64</sup> This is in accordance with the observations of Ruzicka<sup>65</sup> that the essential principles of musk and civet are compounds containing the C=O grouping (macrocyclic ketones). Spontaneous polymerization of cyclic anhydrides on standing, however, is accompanied by a disappearance of their odor.

That  $\alpha$ -anhydrides are linear polymers is indicated by their reaction with aniline to form monoanilide, dianilide, and free acid. With the polyanhydride of adipic acid, for example, this breaking of the molecule may be represented by:<sup>66</sup>



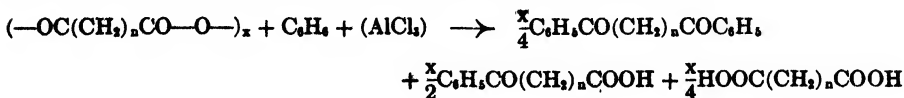
Similar reactions take place with ammonia, diethylamine, and phenol. A general equation for such reactions, which does not consider the end groups, is:



The monomeric anhydride, on the other hand, furnishes only the monoanilide.



In the presence of aluminum chloride, polyanhydrides react with benzene to give dibenzoyl alkane,  $\omega$ -benzoyl fatty acid, and dibasic acid.<sup>67</sup>



In the case of polyesters derived from hexadecamethylene dicarboxylic acid and trimethylene glycol, continuous filaments are made by drawing out the molten ester or by dissolving the ester in chloroform and extruding the solution through a rayon spinneret.<sup>68</sup> The molten ester may be extruded also. In this manner filaments are made which are 0.001 inch in diameter, melt at 74-75°C., and are

<sup>64</sup> J. W. Hill and W. H. Carothers, *J.A.C.S.*, 1933, 55, 5039.

<sup>65</sup> L. Ruzicka, *Helv. Chim. Acta*, 1926, 9, 220, 716, 1006.

<sup>66</sup> J. W. Hill, *J.A.C.S.*, 1930, 52, 4110.

<sup>67</sup> J. W. Hill, *J.A.C.S.*, 1933, 54, 4105.

<sup>68</sup> W. H. Carothers and J. W. Hill, *J.A.C.S.*, 1933, 54, 1579.

opaque and devoid of luster. If, however, tension is applied during spinning then the filaments are transparent and highly lustrous, while their strength and pliability are greatly increased. Reference is made in Chapter 4 to the differences in the x-ray patterns of these types of fibers.

Fibers resembling the above were obtained from the polyesters of  $\omega$ -hydroxydecanoic acid,  $\omega$ -hydroxypentadecanoic acid, ethylene glycol and sebacic acid, trimethylene glycol and adipic acid, and ethylene glycol and succinic acid. Those from polyanhydrides (e.g., sebacic acid anhydride) have a specially high strength, pliability, and luster, though they gradually disintegrate owing to hydrolytic degradation.

Dibasic acids, derived from cyclic or aromatic hydrocarbons, may be the source of polyanhydrides. For example, trans-1,2-dimethylcyclopropane-1,2-dicarboxylic acid is converted by treatment with acetyl chloride into a polymeric non-crystalline anhydride.<sup>66</sup> Also cis-p-hexahydroterephthalic acid reacts with acetic anhydride to give a polymeric cis-anhydride



which at 230°C. changes into the corresponding trans-polyanhydride.<sup>66</sup> Distillation of either polyanhydride of hexahydroterephthalic acid, under reduced pressure with rapid cooling, yields acetic anhydride vapor and the monomeric anhydride. The latter is very unstable and polymerizes when melted or warmed in benzene in the presence of a trace of sodium hydroxide.

#### POLYAMIDES AND MIXED POLYESTER-POLYAMIDES

Amino acids having four or five carbon atoms lose water on heating and yield the corresponding lactams. Thus,  $\gamma$ -aminobutyric acid<sup>70</sup> and  $\delta$ -aminovaleric acid<sup>71</sup> are converted to 5- and 6-membered cyclic lactams, respectively. Under similar conditions, higher amino acids give rise to polymerized compounds.  $\epsilon$ -Aminocaproic acid, for example, furnishes 20-30 per cent of the 7-membered cyclic lactam and 80-70 per cent of a non-distillable, polymerized material of approximately the same composition.<sup>72</sup>  $\xi$ -Aminoheptonic acid on heating undergoes intermolecular reactions resulting in the formation of products<sup>73</sup> which differ in their properties from the 8-membered lactam prepared by other methods.<sup>74</sup>

The mixture of polymer (polyamide) and lactam from  $\epsilon$ -aminocaproic acid is separated by distillation or by extraction with alcohol.<sup>75</sup> The former is a hard gray wax, insoluble in most organic solvents, but can be recrystallized from formamide. Its molecular weight (in phenol) is about 800-1200. It can be quantitatively hydrolyzed to  $\epsilon$ -aminocaproic acid by boiling concentrated hydrochloric acid. Partial hydrolysis yields polyaminocaproylaminocaproic acid. The structure assigned to the polyamide is



Carothers and Hill<sup>76</sup> have pointed out the analogy between this type of polymer and the polyesters obtained by self-esterification of higher hydroxyacids or from the action of glycols on dibasic acids. In the first instance the binding agent be-

<sup>66</sup> K. von Auwers and O. Ungernach, *Ann.*, 1934, 511, 152.

<sup>67</sup> R. Malachowski and J. Jankierwiesowna, *Ber.*, 1934, 67, 1783.

<sup>68</sup> S. Gabriel, *Ber.*, 1899, 22, 3335.

<sup>69</sup> C. Shotten, *Ber.*, 1888, 21, 2235.

<sup>70</sup> J. von Braun, *Ber.*, 1907, 40, 1834. S. Gabriel and T. A. Maas, *Ber.*, 1899, 32, 1266.

<sup>71</sup> A. Manasse, *Ber.*, 1902, 35, 1867. J. von Braun, *loc. cit.*

<sup>72</sup> O. Wallach, *Ann.*, 1899, 309, 18; 1900, 312, 205.

<sup>73</sup> W. H. Carothers and G. J. Berchet, *J.A.C.S.*, 1930, 52, 5289.

<sup>74</sup> W. H. Carothers and J. W. Hill, *J.A.C.S.*, 1933, 54, 1546.

tween the units is  $\text{—O—}$ , and in the latter is  $\text{—NH—}$ . The polyamides are, in general, harder, tougher, less easily fusible, and much less soluble than polyesters. Similar to the changes observed with polyanhydrides, the polyamide when heated for 48 hours at  $200^{\circ}\text{C}$ . in a molecular still was transformed to a volatile cyclic lactam which is a harder and tougher material and in thin sections is plastic and flexible.

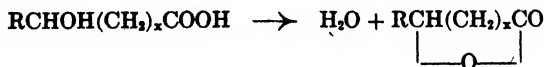
The same investigators attempted the preparation of mixed polyester-polyamides. The polyesters previously noted are not entirely satisfactory for the manufacture of synthetic silk owing to their low melting points and considerable solubility in organic solvents. The polyamide, on the other hand, is too infusible and insoluble for use in making fibers. The mixed polyester-polyamides were intended as a compromise between these two extremes.

Such compounds were obtained by heating mixtures of trimethylene glycol, hexadecamethylene dicarboxylic acid, and  $\epsilon$ -aminocaproic acid for three hours at  $200\text{--}220^{\circ}\text{C}$ . The glycol and acid were present in equivalent proportions, and amounts of amino acid varied from 1 to 5 mols per mol of the dibasic acid. Heating was continued for 5 hours more at 1 mm. pressure at  $250\text{--}260^{\circ}\text{C}$ . and the viscous residue then was transferred to a molecular still and heated for three days at  $200^{\circ}\text{C}$ . As the proportion of amino acid was increased the polymers increased in brittleness, hardness, transparency and melting point, but their solubility diminished. Polymers containing the higher proportions of amino acids were insoluble in ethyl acetate: with less of the acid the compounds dissolved in this solvent. Since the polyamide itself is insoluble in hot ethyl acetate, the mixed polyester-polyamides cannot have been merely physical mixtures. These mixed compounds could be drawn into strong, pliable transparent fibers which were superior to those from the polyester alone.

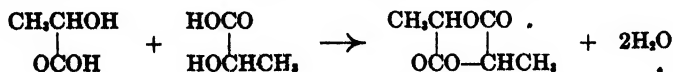
Abderhalden and Reich<sup>77</sup> found that  $\beta$ -alanine methyl ester, when kept for a few days, yielded a white amorphous solid, insoluble in ether, and decomposing at  $310^{\circ}\text{C}$ . Molecular weight determinations indicated a 5-fold polymerization. In the preparation of hexamethylenimine by treating 6-bromo-*n*-hexylamine,  $\text{NH}_2(\text{CH}_2)_6\text{Br}$ , with alkali and distilling with steam, an amorphous residue of the composition  $(\text{C}_6\text{H}_{12}\text{N})_n$  is obtained.<sup>78</sup>

#### LACTONE FORMATION

Lactone formation is of importance in the chemistry of resins, an example of a naturally occurring product of this type being shellac. Lactones, or inner esters, are obtained by the elimination of water between a hydroxyl group and a carboxyl group, both of which are in the same molecule. With  $\gamma$ - or  $\delta$ -hydroxyacids the reaction can be represented by:



Closely related to this type of compounds are lactides, or cyclic esters, resulting from the elimination of water between hydroxyl and carboxyl groups in two molecules of an  $\alpha$ -hydroxy acid. For lactic acid this can be illustrated as follows:



When the carboxyl and hydroxyl groups are widely separated, lactone formation is accompanied by the development of other products. Thus,  $\epsilon$ -hydroxyacids give

<sup>77</sup> E. Abderhalden and F. Reich, *Z. physiol. Chem.*, 1928, 178, 169; *Brit. Chem. Abs. A*, 1929, 52.

<sup>78</sup> J. von Braun and O. Goll, *Ber.*, 1927, 60, 1833; *Chem. Abs.*, 1927, 21, 3156.

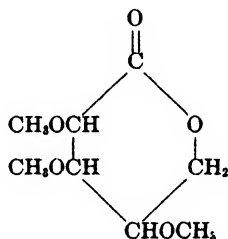


lactones and polyesters (polylactones)<sup>79</sup> and  $\omega$ -hydroxyacids yield almost exclusively polyesters.<sup>80</sup> Lactones of high molecular weight can be made by oxidation of the corresponding ketone.<sup>81</sup> The slow addition of sodium persulphate (in sulphuric acid) to a cold solution of civetone in benzene resulted in an emulsion containing a resin, together with a small amount of a petroleum-ether-soluble lactone.<sup>82</sup>

Many lactones, particularly six-membered cyclic esters, are known to polymerize with ease, and depolymerize (reversible polymerization) on heating. Carothers, Dorough, and Van Natta<sup>83</sup> have drawn attention to such instances.

$\delta$ -Valerolactone,  $\text{CH}_2 \begin{array}{c} \text{CH}_2\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ , which is initially a mobile oil, gradually thick-

ens, and finally solidifies to a crystalline mass, which proves to be a 5- to 7-fold polymer.<sup>84</sup> The partial decomposition of this lactone as it approaches its boiling point has been attributed to the formation of a polymer.<sup>85</sup> Drew and Haworth<sup>86</sup> observed the polymerization of the crystalline lactone of 2,3,4-trimethyl-l-arabonic acid,



in the presence of a trace of hydrogen chloride and its depolymerization on heating. Bischoff<sup>87</sup> noted the reversible polymerization of ethylene oxalate,  $\text{CH}_2 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \begin{array}{c} \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{CO}$ , prepared from ethylene glycol and monoethyl oxalate.

Extending these observations on the reversible polymerization of 6-membered rings, Carothers and his co-workers found that substituting groups generally reduced the tendency for such molecules to polymerize. Thus,  $\delta$ -valerolactone was completely polymerized to a waxy solid on standing for 29 days at room temperature.  $\alpha$ -n-Propyl- $\delta$ -valerolactone remained unchanged for 1 year at room temperature or at 80°C. for one month. Under the latter conditions addition of a trace of potassium carbonate or zinc chloride caused the lactone to become viscous and its apparent molecular weight to rise to 1100-1200. On the other hand, the lactide of  $\alpha$ -hydroxypropionic acid (lactic acid) was transformed in two hours at 250-275°C. to a resinous mass with a molecular weight of about 3000. In the presence of potassium carbonate polymerization took place at 140-150°C.

The effect of substituting groups is shown also by the work of Palomaa and Toukola.<sup>88</sup> They report that  $\gamma$ -hydroxypropoxyacetic acid, at 200-220°C. and

<sup>79</sup> A. von Baeyer and O. Seuffert, *Ber.*, 1899, 32, 3624. E. E. Blaise and A. Koehler, *Compt. rend.*, 1909, 148, 1772; *J.C.S.*, 1909, 96 (1), 551. C. S. Marvel, D. W. MacCorquodale, F. E. Kendall and W. A. Lauer (*J.A.C.S.*, 1924, 46, 2835) report that in the preparation of  $\epsilon$ -hydroxycaproic acid from the corresponding bromide a mixture of the acid and lactone was obtained.

<sup>80</sup> W. H. Lycan and R. Adams, *J.A.C.S.*, 1929, 51, 625, 3450.

<sup>81</sup> L. Ruzicka and M. Stoll, *Helv. Chim. Acta*, 1929, 12, 4634; *Chem. Abs.*, 1929, 23, 1110.

<sup>82</sup> M. Stoll and R. E. Gardner, *Helv. Chim. Acta*, 1934, 17, 1609; *Chem. Abs.*, 1935, 29, 2148.

<sup>83</sup> W. H. Carothers, G. L. Dorough and J. Van Natta, *J.A.C.S.*, 1932, 54, 761.

<sup>84</sup> F. Fichter and A. Beisswenger, *Ber.*, 1903, 36, 1200.

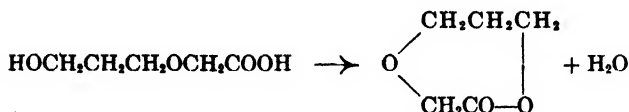
<sup>85</sup> R. W. Thomas and H. A. Schuette, *J.A.C.S.*, 1932, 54, 3008.

<sup>86</sup> H. D. K. Drew and W. N. Haworth, *J.C.S.*, 1927, 775.

<sup>87</sup> Bischoff, *Ber.*, 1907, 40, 2808.

<sup>88</sup> M. H. Palomaa and N. Toukola, *Ber.*, 1933, 66, 1629.

0.1-1 mm. pressure, passes into the corresponding lactone which is not polymerized.



Furthermore, this lactone is hydrolyzed (in acid solution) only about 1/90 as

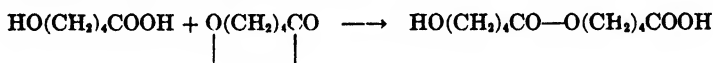
fast as the homologous compound,  $\begin{array}{c} \text{CH}_2\text{CH}_2 \\ \diagup \quad \diagdown \\ \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{CH}_2\text{CO} \end{array}$ , which has one less  $\text{CH}_2$  group.

Lycan and Adams<sup>20</sup> synthesized intermolecular esters by heating  $\omega$ -hydroxyacids, the molecular weights of the esters varying from 1000 to 9000. Carothers and Van Natta<sup>21</sup> similarly prepared polyesters (molecular weights ranging from 780 to 25,000) from  $\omega$ -hydroxydecanoic acid.<sup>21</sup> Strong, oriented fibers were obtained from polyesters of molecular weights greater than 9330. Maximum tensile strength, 13.1 kg. per sq.mm. (ca. 18,500 lbs. per sq. in.), was exhibited by fibers with a molecular weight of 16,900.

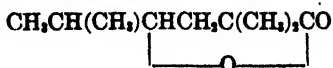
Carothers<sup>22</sup> further suggests that the polymers are linear polyesters having a chain structure of the type



It seems probable that the first step in the polymerization of cyclic esters (lactones) involves the intervention of a trace of the corresponding hydroxy acid. This reacts with the lactone to give the dimeric acid. The latter in turn yields a trimeric acid, and reaction continues until all the lactone is exhausted or the chains become too long for further reaction. In the case of  $\delta$ -valerolactone, the first stage in polymerization may be represented by:



Crude  $\epsilon$ -hydroxycaproic acid (containing some of the corresponding lactone) on being heated to 150-210°C. gave  $\epsilon$ -caprolactone, and a small proportion (about 1 per cent) of the dimeric, cyclic self-ester of  $\epsilon$ -hydroxycaproic acid.<sup>23</sup> When kept in a sealed tube for 12 hours at 150°C., the lactone slowly became more viscous and, on cooling, solidified to a solid mass. A trace of potassium carbonate reduced the heating time to about 5 hours. The lactone, dimer, and polyester were derivatives of  $\epsilon$ -hydroxycaproic acid and no shift of the hydroxyl oxygen was involved in their formation. Coucoulesco<sup>24</sup> reports that a trimethyl hydroxycaproic acid,  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CHOHCH}_2\text{C}(\text{CH}_3)_2\text{COOH}$ , when distilled from dilute sulphuric yielded a white amorphous resin, possibly the polymerized lactone,



An important contribution to the chemistry of hydroxy acids is that of Chuit

<sup>20</sup> W. H. Lycan and R. Adams, *J.A.C.S.*, 1929, 51, 3450.

<sup>21</sup> W. H. Carothers and F. J. Van Natta, *J.A.C.S.*, 1933, 55, 4714.

<sup>22</sup> For the determination of molecular weights of polymerized  $\omega$ -hydroxydecanoic acid by ultracentrifugal analysis, see E. O. Kraemer and W. D. Lansing, *J.A.C.S.*, 1933, 55, 4319. E. O. Kraemer and F. J. Van Natta, *J. Phys. Chem.*, 1932, 36, 2178.

<sup>23</sup> Cf. W. H. Carothers and F. J. Van Natta, *J.A.C.S.*, 1930, 52, 314.

<sup>24</sup> F. J. Van Natta, J. W. Hill, and W. H. Carothers, *J.A.C.S.*, 1934, 56, 455.

<sup>25</sup> I. Coucoulesco, *Bull. soc. chim. Roumanie*, 1923, 5, 63; *Chem. Abs.*, 1924, 18, 1469.

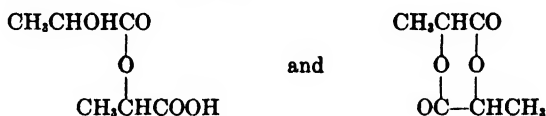
and Hausser,<sup>95</sup> who synthesized and studied the properties of hydroxy fatty acids containing 8-21 carbon atoms. Several derivatives of these acids were isolated from waxes extracted from conifers.

Resinification of mandelic acid was noted by Ipatiev and Rasuvajev<sup>96</sup> when they attempted to hydrogenate this acid in the presence of a nickel catalyst. Brittle resins, apparently lactides, result from the thermal decomposition of 4-carboxy-2,6-dimethylmandelic acid<sup>97</sup> and of benzilic acid.<sup>98</sup>

### LACTIC ACID

This acid is of interest in connection with synthetic resins not only because of its yielding lactides when heated but also because it may be employed in resinification studies.

Commercial lactic acid contains about 75 per cent of acid, whose constitutional formula is  $\text{CH}_3\text{CHOHCOOH}$ , together with about 8 per cent of its anhydrides whose formulas can be represented by



The former is a monoanhydride and the latter a dianhydride or lactide. Hydrolysis of anhydride and lactide occurs with formation of lactic acid when either substance is heated with water or acid or alkaline aqueous solutions. A method for the analysis of mixtures of lactic acid and its anhydrides is described by Thurmond and Edgar.<sup>99</sup>

Wislicenus<sup>100</sup> reported that the anhydride obtained by heating lactic acid in a current of air at 130°C. was a light-yellow, amorphous body, slightly soluble in water and very soluble in alcohol or ether. The lactide has been described as a white, crystalline solid, very slightly soluble in alcohol or ether,<sup>101</sup> and is formed at a higher temperature than that required for the anhydride, namely 200°C.

The reaction of lactic acid, as well as its acid or basic sodium, calcium and barium salts, with water at 200-450°C. under pressure was investigated by Fischer, Schrader, and Wolter.<sup>102</sup> The acid yielded acetaldehyde, together with acetone and resins, and very little alcohol was formed. In addition, considerable quantities of carbon monoxide, hydrogen, unsaturated hydrocarbons, methane, and ethane were produced. From the salts, however, 15-20 per cent of alcohol was obtained, except from a basic sodium lactate which gave only a trace of alcohol. Krauskopf and Carter<sup>103</sup> noted that barium lactate could be crystallized from a solution containing barium hydroxide, whereas a neutral solution or one containing free lactic acid could be evaporated to a thick syrup and in some instances to a glass-like solid without the formation of crystals. The amorphous material was shown to have the same composition as the crystalline lactate. Lactates of other metals, especially the more electropositive ones, behaved similarly; for example, crystal-

<sup>95</sup> P. Chuit and J. Hausser, *Helv. Chim. Acta*, 1920, 12, 463; *Chem. Abs.*, 1920, 23, 3063.

<sup>96</sup> V. Ipatiev and G. Rasuvajev, *Ber.*, 1926, 59, 306.

<sup>97</sup> W. H. Perkin and R. A. B. Tapley, *J.C.S.*, 1924, 125, 2428.

<sup>98</sup> B. L. Vansetti, *Atti. II congresso nas. chim. pura applicata*, 1926, 1928; *Chem. Abs.*, 1928, 22, 2162.

<sup>99</sup> G. I. Thurmond and G. Edgar, *Ind. Eng. Chem.*, 1924, 16, 823.

<sup>100</sup> J. Wislicenus, *Ann.*, 1873, 164, 181; 1873, 167, 302. See also J. Pelouse, *Ann.*, 1846, 53, 114; Engelhardt, *Ann.*, 1849, 70, 242.

<sup>101</sup> F. Kraft and W. A. Dyes, *Ber.*, 1895, 28, 2589. See also J. Gay-Lussac, *Ann.*, 1833, 7, 43; J. Pelouse, *loc. cit.*; Engelhardt, *loc. cit.*

<sup>102</sup> F. Fischer, F. Schrader, and H. Wolter, *Gas. Abhandl. Kennt. Kohle*, 1921, 6, 99.

<sup>103</sup> F. C. Krauskopf and A. S. Carter, *J.A.C.S.*, 1926, 48, 1474.

line lactates of the alkali metals could not be obtained. The lactide anhydride was shown to inhibit crystallization, its probable mode of action being that of a protective colloid.

**Resins from Lactic Acid.** A resin is obtained by refluxing 90 per cent lactic acid for several hours and then removing the volatile portion by distillation.<sup>106</sup> The product is light yellow in color, melts at 30-35°C., is soluble in acetone, alcohol, and other organic solvents, and is miscible with cellulose acetate. Lacquers in which this resin is incorporated yield clear, hard films which possess the property of sticking to various surfaces. The lactic acid resin (together with cellulose acetate) has been considered also in the manufacture of laminated glass,<sup>105</sup> and as an adhesive for making composite sheets from thin films of cellulose derivatives by heat and pressure.<sup>106</sup>

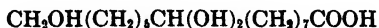
Zimmermann<sup>107</sup> heats lactic acid *in vacuo*, raising the temperature slowly from 100 to 200°C., and condenses the product with formaldehyde or paraldehyde. An odorless, non-inflammable, resinous product, soluble in chloroform or glacial acetic acid, and slightly soluble in benzene, is thus obtained. Its color varies from pale yellow to almost black, according to the purity of the lactic acid employed.

#### RELATED PRODUCTS

After heating glycolic acid very gradually to 150°C., maintaining it at this temperature for several hours, and then cooling, a hard compact mass is obtained.<sup>108</sup> This substance possesses unusual adhesive properties, a strength of 1 ton per square inch being obtained when it was applied to very smooth (but not optically polished) surfaces. In this respect "overheated" glycolic acid compares favorably with many other adhesives such as marine glue, high-grade rosin, ester gum, and Bakelite "A." In the preparation of resins from formaldehyde and phenol with sodium hydroxide solution as a catalyst, the addition of glycerol esters of lactic acid yields a clearer product.<sup>109</sup>

#### ARTIFICIAL SHELLAC

The problem of the constitution of natural shellac thus far is unsolved. Harries and Nagel,<sup>110</sup> however, isolated some degradation products of the natural resin and from an examination of these concluded that shellac is a mixture of substances obtained by the lactide condensation of various hydroxy-carboxylic acids. Two acids in particular were isolated: aleuritic acid, whose formula is probably<sup>111</sup>



and shellolic acid (shellenedioldicarboxylic acid) for which the formula

<sup>104</sup> W. H. Moss, U. S. P. 1,849,107 and 1,849,108, Mar. 15, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 2879. Canadian P. 319,148, 1932, to Camille Dreyfus; *Chem. Abs.*, 1932, 26, 2072. W. H. Moss and C. Dreyfus, British P. 311,657, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 981.

<sup>105</sup> W. H. Moss, U. S. P. 871,725, Aug. 16, 1932, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 6090.

<sup>106</sup> British P. 354,280, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1933, 27, 383.

<sup>107</sup> E. Zimmermann, German P. 305,775, 1917; *J.S.C.I.*, 1919, 36, 187A.

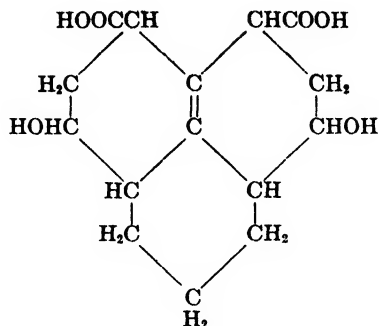
<sup>108</sup> *Improved Adhesives for Industry*. Final Report of the Adhesives Research Committee, *Chem. Age (London)*, 1932, 27, 167.

<sup>109</sup> French P. 703,251, 1930, to "Herold" A.-G.; *Chem. Abs.*, 1931, 25, 4422.

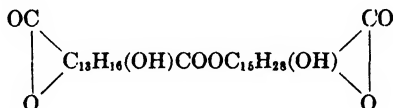
<sup>110</sup> C. Harries and W. Nagel, *Ber.*, 1923, 55, 3833; *Kolloid-Z.*, 1923, 33, 247; *J.S.C.I.*, 1923, 42, 1234A; *Wiss. Veröff. Siemens-Konz.*, 1924, 3, 12; *J.C.S.*, 1924, 126 (1), 975. C. Harries, *Ber.*, 1923, 56, 1048.

<sup>111</sup> W. Nagel and M. Kornichen, *Wiss. Veröff. Siemens-Konz.*, 1927, 6, 235; *Brit. Chem. Abs. B*, 1928, 578. The effect of small amounts of impurities on the properties of shellac is discussed by W. H. Gardner, *Ind. Eng. Chem.*, 1933, 25, 550.

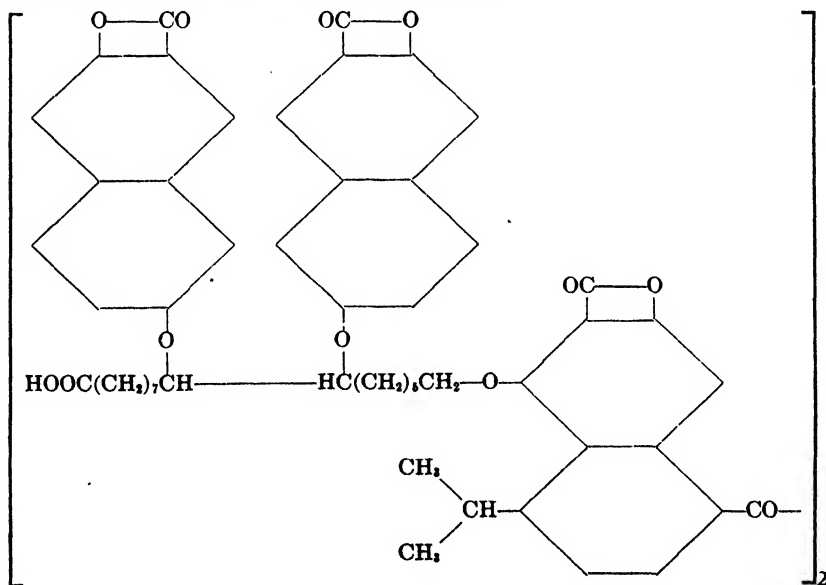
<sup>112</sup> A. Tschirch and A. Farmer (*Arch. Pharm.*, 1890, 237, 39; *J.C.S.*, 1890, 76 (1), 446) suggest that aleuritic acid is a dihydroxyundecic acid.



is suggested. Heating mixtures of these two acids (in varying molecular proportions) under reduced pressure at 150-160°C. yielded yellow, liquid lactides, which on cooling became yellow resinous masses. Harder and more infusible resins were produced by using temperatures above 200°C. A possible formula for one of the simpler components of shellac is



Another structure<sup>112</sup> suggested for lac resin is



which is based on the assumption that pure lac resin consists of 30 per cent of aleuritic acid, 10 per cent shellolic acid and 60 per cent unknown hydroxy acids similar to shellolic acid. In the above formula shellolic acid is considered to be a reduced dihydroxyisopropyl naphthalene dicarboxylic acid.

<sup>112</sup> W. Nagel and E. Baumann, *Wiss. Veröff. Siemens-Konz.*, 1923, 11, 99; *Brit. Chem. Abs. B*, 1923, 30.

Bhattacharya<sup>112</sup> isolated a shellolic acid which differed in many respects from that described by Nagel. A comparison of the two acids is given in Table 52.

TABLE 52.—*Characteristics of Shellolic Acid.*

	Nagel 200-201°C. (decomp.) Non-hygroscopic	Bhattacharya 90-91°C. Hygroscopic
Melting Point		
Mol. wt. (from sap. val.)	297	298
Zn content of Zn salt	17.85%	17.6%
Analysis by combustion	$C_{11}H_{20}O_6$	$C_{11}H_{20}O_6-H_2O$
$[\alpha]_D^{25}$	32.6°	30°
M. p. of Methyl Ester	149°C.	Viscous liquid
M. p. of Hydrazide	243-244°C.	131°C.
M. p. of p-Bromophenacyl ester	...	175-176°C.

The formula  $C_{11}H_{20}O_6-H_2O$  indicates that combustion values were in agreement with those for the lactone  $C_{11}H_{20}O_6$ . Lactone formation was verified by the differences in acid and saponification values. According to Bhattacharya, shellolic acid possesses a condensed three-benzene-ring structure in which the orientation of the carboxyl and hydroxyl groups has not yet been determined.

Although shellac is insoluble in aqueous solutions of alkali bicarbonates it does dissolve in solutions of alkali carbonates, thus possibly indicating the presence of phenolic groups.<sup>114</sup> Furthermore, molecular weight determinations and analyses of the heavy-metal salts of shellac lead to the conclusion that the resin molecules are dibasic acids. Gardner and Whitmore<sup>115</sup> report that the best solvents for shellac are alcohols, ketones, and organic acids. Since many substances are often more soluble in those solvents related to them structurally,<sup>116</sup> the indications are that hydroxyl, carbonyl, and carboxyl groups are present in shellac. Because of the insolubility of shellac in ethylene glycol and glycerol, it is believed also that the hydroxyl groups in aleuritic acid are involved in some other grouping, e.g., that of a lactide.

In synthesizing shellac-like resins, lactic, glyceric, dihydroxy-, trihydroxy-, or tetrahydroxy-stearic acids, or the oxidation products from linseed oil acids may be substituted for aleuritic acid. As the second component, in place of shellolic acid, cyclohexanocarboxylic acids, tetrahydronaphthoic acid, or their hydroxy derivatives may be employed. On heating mixtures of these acids, resins resembling shellac are obtained.<sup>117</sup> In a similar manner copals and polyhydroxy fatty acids give shellac substitutes.<sup>118</sup>

Scheiber and Noack<sup>119</sup> found that resin formation generally resulted from the interaction of aliphatic oxycarboxylic acids (e.g., those from the moderate oxidation of unsaturated fatty acids) with hydroaromatic oxycarboxylic acids (such as oxidized resin oil acids). To illustrate, 100 parts of oxidized soluble Manila copal, 100 parts of oxidized rosin, and 25 parts of castor oil acids are heated gradually to 200°C. The resinous product is soluble in alcohol, alkali carbonate and borax solutions, and insoluble in hydrocarbons and fatty oils. Variations of this procedure consist in the substitution of one of the components by chlorinated derivatives<sup>120</sup> (for example, a mixture of trihydroxystearic acid and chlorinated abietic acid) or in the chlorination

<sup>112</sup> R. Bhattacharya, *J.S.C.I.*, 1935, 54, 83T.

<sup>114</sup> W. H. Gardner, W. F. Whitmore and H. J. Harris, *Ind. Eng. Chem.*, 1933, 25, 696.

<sup>115</sup> W. H. Gardner and W. F. Whitmore, *Ind. Eng. Chem.*, 1929, 21, 226.

<sup>116</sup> For an application of this rule to the solubility of nitrocellulose and various gums in lacquer solvents, see B. K. Brown, *Ind. Eng. Chem.*, 1928, 20, 183.

<sup>117</sup> German P. 440,375, 1922, to Siemens & Halske A.-G.; *Brit. Chem. Abs.* B, 1928, 867. Cf. W. Nagel and W. Hüller, *Fettechem. Umschau*, 1933, 40, 49; *Chem. Abs.*, 1933, 27, 2589.

<sup>118</sup> W. Dux, British P. 350,764, 1930; *Brit. Chem. Abs.* B, 1931, 818.

<sup>119</sup> J. Scheiber and W. Noack, U. S. P. 1,660,094, Feb. 21, 1928; *Brit. Chem. Abs.* B, 1928, 276. *Brit. P.* 242,715, 1925; *Chem. Abs.*, 1927, 21, 2590.

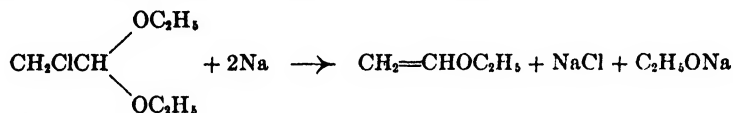
<sup>120</sup> J. Scheiber, U. S. P. 1,903,598, Apr. 11, 1933, to W. Dux; *Brit. Chem. Abs.* B, 1933, 1021.

of a mixture of unsaturated fatty acids and resinolic acids<sup>121</sup> and effecting condensation by heating.<sup>122</sup> Anhydrous metallic chlorides (zinc or aluminum chloride) serve as catalysts

The formation of synthetic resins as described above apparently entails a lactide condensation in each instance and offers a close parallel with the case of natural shellac. Of a somewhat different nature is the production of resins by polymerization of benzyl and cinnamic alcohols by such agents as sulphuric or phosphoric acid, or phosphorus pentoxide. The reaction mixture is heated first to 130° and then to 180°C. An alternative procedure is to heat a mixture of phosphoric acid, an aromatic hydrocarbon, and formaldehyde, the latter two components forming an alcohol *in situ* which is then polymerized. Resins so obtained are soluble in organic solvents and may be employed in paints and varnishes.<sup>123</sup>

### VINYL ETHERS

Although vinyl alcohol,  $\text{CH}_2=\text{CHOH}$ , has not yet been isolated because of its instability, nevertheless a number of its derivatives are known and of these the vinyl ethers are of considerable importance owing to their tendency to polymerize. Vinyl ethyl ether,  $\text{CH}_2=\text{CHOC}_2\text{H}_5$ , was described first by Wislicenus<sup>124</sup> who made it by the action of sodium on chloroacetal.



Claisen's<sup>125</sup> method of preparation depends upon the removal of alcohol from diethyl acetal,  $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$ , by phosphorus pentoxide in the presence of quinoline. Vinyl and other unsaturated ethers may be obtained by passage of the vapors of aliphatic or aromatic acetals (with or without a diluent) over metals, such as silver, gold, or platinum, at temperatures of 200–350°C. Other metals, oxides, phosphates, or silicates may be added to the catalysts.<sup>126</sup>

Further procedures involve dissolving acetylene (or its homologues) under pressure in sulphuric acid at 0° to –15°C., using mercuric sulphate as a catalyst, and reacting the acid sulphate with alcohol.<sup>127</sup> Hydroxylated compounds, which do not contain groups sensitive to alkalies, are reported to combine with acetylene, at temperatures of 80–250°C. in strongly alkaline media.<sup>128</sup> In this way it is possible to prepare the ethyl vinyl ether of ethylene glycol (b.p. 126°C.) from the monoethyl ether of ethylene glycol, as well as the monovinyl ether of diethanolamine, and vinyl octyl ether.

<sup>121</sup> Resinolic acids are those acids occurring in natural resins: A. H. Allen, "Commercial Organic Analysis," P. Blakiston's Son & Co., Philadelphia, 1907, 2, 143. R. S. Morrell, "Varnishes and Their Components," Henry Froude and Holde & Stroughton, London, 1923, 107. See also Chapter 56.

<sup>122</sup> J. Scheiber, U. S. P. 1,927,472, Sept. 19, 1933.

<sup>123</sup> R. P. L. Britton, British P. 269,973, 1926, to Griffiths Bros. & Co., Ltd.; *Chem. Abs.*, 1928, 22, 1486.

<sup>124</sup> J. Wislicenus, *Ann.*, 1878, 192, 100. Note also Chapters 51 and 52.

<sup>125</sup> L. Claisen, *Ber.*, 1898, 31, 1019.

<sup>126</sup> British P. 245,255, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 156. Cf. W. O. Herrmann and H. Deutsch, U. S. P. 1,903,169, Mar. 21, 1933, to Consortium für Elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 3222. French P. 710,603, 1931; *Chem. Abs.*, 1932, 26, 1616. German P. 560,354, 1930; *Chem. Abs.*, 1933, 27, 993.

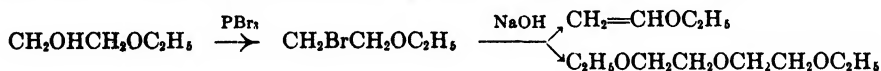
<sup>127</sup> H. Plauson and J. A. Vielle, British P. 155,121, 1920; *Chem. Abs.*, 1921, 15, 1728. H. Plauson, U. S. P. 1,426,288, Nov. 31, 1922; *Chem. Abs.*, 1923, 17, 504. German P. 333,281, 1921, to Plauson's Forschungsinstitut G.m.b.H.; *Chem. Abs.*, 1923, 17, 1804.

<sup>128</sup> W. Reppe, U. S. P. 1,959,927, May 22, 1934; *Chem. Abs.*, 1934, 28, 4431. German P. 584,240, 1933; *Chem. Abs.*, 1934, 28, 1038. French P. 724,955, 1931; *Chem. Abs.*, 1932, 26, 4325. All patents to I. G. Farbenind. A.-G.

Ernst and Berndt<sup>120</sup> suggest treating aromatic hydroxy compounds with vinyl halides (particularly the chlorides) in the presence of bases and, optionally, of catalysts. Phenol, sodium hydroxide, water, and vinyl chloride, for example, when fused together at 180-200°C. gave an 80 per cent yield of vinyl phenyl ether. Reaction of vinyl monohalides with alcoholates or phenylates, in the presence of a solvent, or with mixtures of alcohols and oxides or hydroxides of alkali or alkaline earth metals, also furnishes vinyl ethers.<sup>120</sup> Ethylene or ethylidene dihalides may be employed in a similar manner. To illustrate, ethylene dichloride and sodium ethoxide form ethyl vinyl ether, while vinyl cyclohexyl ether (b.p. 147-148°C.) is obtained from cyclohexanol, sodium hydroxide, and ethylene dibromide.<sup>121</sup>

Unsaturated ethers of nuclear-methylated hydroxybenzyl alcohol have been prepared by Melamid<sup>122</sup> by treating the alcohols obtained from m- and p-cresol and formaldehyde with a caustic alkali solution (20 per cent) and an allyl halide. Oily compounds are derived which solidify by absorption of oxygen and consequently are applicable as drying oils. Similar products were obtained by employing anthracene oil in place of cresols,<sup>123</sup> the alkali-soluble constituents reacting to form ethers.

Chalmers<sup>124</sup> describes the conversion of alkyl  $\beta$ -bromoethyl ethers into vinyl derivatives by treatment with solid sodium hydroxide. The bromoethers are prepared by the action of phosphorus tribromide on the corresponding glycol monoethers and then distilled in the presence of the alkali. During distillation vinyl ethers and dialkylethers of diethylene glycol are formed simultaneously.



The physical constants for some vinyl ethers are given in Table 53.

TABLE 53.—Physical Constants of Vinyl Ethers.

Ether	Boiling Point, °C.	Density (D <sub>4</sub> <sup>20</sup> )	Refractive Index (n <sub>D</sub> <sup>20</sup> )
Vinyl methyl.....	12-14°	.....	.....
Vinyl ethyl.....	35.5°	0.7589	1.3856 (n <sub>D</sub> <sup>25</sup> )
Vinyl n-butyl.....	93.3°	0.7887	1.4026
Vinyl $\beta$ -chloroethyl ....	108.0°	1.044	1.4362
Vinyl phenyl.....	155.5°	0.9776	1.5226

Divinyl ether is prepared by the action of heated caustic alkali on  $\beta$ , $\beta'$ -dichloroethyl ether.<sup>125</sup> Best yields and smaller proportions of by-products (acetaldehyde, dioxane, ethylene oxide, and  $\beta$ -chloroethyl vinyl ether) are secured when the temperature is 200-250°C. and the alkali is stirred to prevent its surface from becoming coated with alkali chloride.<sup>126</sup> The ether boils at about 23°C.

Phenyl vinyl ether (b.p. 155-156°C.) is obtained by heating  $\beta$ -bromophenetole,  $\text{C}_6\text{H}_5\text{OCH}_2\text{CH}_2\text{Br}$ , with anhydrous potassium hydroxide.<sup>127</sup> Another method of

<sup>120</sup> O. Ernst and W. Berndt, German P. 513,679, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 1841.

<sup>121</sup> British P. 332,605, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 302. W. Reppe, German P. 550,403, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4825.

<sup>122</sup> British P. 341,074, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4891. See also W. Reppe, U. S. P. 1,941,108, Dec. 26, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1357. German P. 550,495, 1929 and 559,523, 1930; *Chem. Abs.*, 1932, 26, 4825; 1933, 27, 736.

<sup>123</sup> M. Melamid, German P. 352,003, 1920; *J.S.C.I.*, 1922, 41, 728A.

<sup>124</sup> M. Melamid, German P. 370,083, 1920; *J.S.C.I.*, 1923, 42, 597A.

<sup>125</sup> W. Chalmers, *Can. J. Research*, 1932, 7, 464; *Chem. Abs.*, 1933, 27, 701.

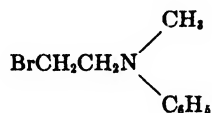
<sup>126</sup> H. Hiibbert, S. Z. Perry and K. A. Taylor, *J.A.C.S.*, 1929, 51, 1551.

<sup>127</sup> W. L. Ruigh and R. T. Major, *J.A.C.S.*, 1931, 53, 2662.

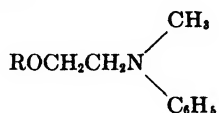
<sup>128</sup> A. Wohl and E. Berthold, *Ber.*, 1910, 43, 2175. The preparation of eugenyl vinyl ether and guaiacyl vinyl ether by analogous methods is described also.



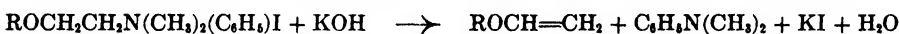
preparing aromatic vinyl ethers consists in converting  $\beta$ -halogenated ethyl aromatic amines, such as



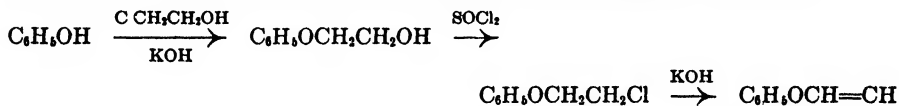
to the corresponding ethers, e.g.,



afterwards forming the quarternary salts by reaction with methyl iodide or sulphate, and decomposing the salt with alkali.<sup>120</sup> The last reaction, which apparently occurs only when R is an aromatic group, may be represented by:



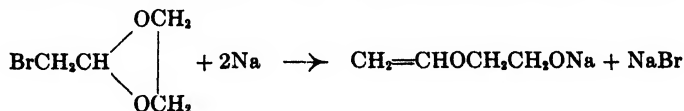
Lauer and Spielman<sup>120</sup> suggest the following procedure: The phenol is transformed to the corresponding hydroxy ether, which is chlorinated with thionyl chloride, and hydrogen chloride then eliminated with potassium hydroxide.



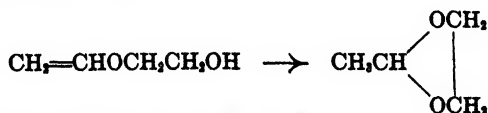
Powell and Adams<sup>140</sup> report that thermal decomposition of phenyl vinyl ether (12 hours at 260-280°C.) leads to the formation of some phenol. Lauer and Spielman<sup>141</sup> found that this ether when heated for 3 hours at 295-300°C. gives only a small proportion of phenol, some acetaldehyde diphenyl acetal  $\text{CH}_3\text{CH}(\text{OC}_6\text{H}_5)_2$ , and a tarry residue. The acetal appeared to result from the interaction of phenol (formed by decomposition of the ether) and phenyl vinyl ether.



Hydroxyethyl vinyl ether is prepared by the action of sodium on bromoethylidene glycol and hydrolysis of the sodium derivative thus formed.<sup>142</sup>



The ether is a colorless oil, boiling at 140°C., soluble in water, ether, and benzene, but insoluble in ligroin. Traces of strong acids (sulphuric or hydrochloric) effect an instantaneous and almost explosive rearrangement of the ether to the cyclic acetal, ethyldene glycol.



<sup>120</sup> J. von Braun and G. Kirschbaum, *Ber.*, 1920, 53, 1399.

<sup>120</sup> W. M. Lauer and M. A. Spielman, *J.A.C.S.*, 1933, 55, 1572.

<sup>140</sup> S. G. Powell and R. Adams, *J.A.C.S.*, 1920, 42, 646.

<sup>141</sup> W. M. Lauer and M. A. Spielman, *loc. cit.*

<sup>142</sup> H. S. Hill and L. M. Pidgeon, *J.A.C.S.*, 1923, 50, 2718. *Cf.* J. Wislicenus, *Ann.*, 1878, 192, 112.

The benzoate of hydroxyethyl vinyl ether, however, does not undergo a similar transformation, indicating that the hydroxyl group plays a specific role in the reaction. Hydroxypropyl vinyl ether, prepared in a similar manner from bromoethylidene trimethylene glycol, exhibits analogous properties.<sup>144</sup>

$\alpha$ - and  $\beta$ -Unsaturated, substituted ethers<sup>144</sup> were produced by passing hydrogen chloride into a mixture of an aldehyde and an alcohol to secure the chloro ether. Bromination, followed by treatment with the Grignard reagent, resulted in  $\beta$ -bromo ethers. These yielded vinyl derivatives on distillation over potassium hydroxide. For example, from  $\alpha$ ,  $\beta$ -dibromoethyl ether was obtained  $\alpha$ -ethoxystyrene (b.p. 109-112°C. at 30 mm.).



The substituted vinyl ethers hydrolyze under the influence of a trace of acid to the corresponding acetone (in the above case acetophenone).

Halogenated vinyl ethers are made by the action of zinc on halogenated derivatives of ethyl ether.<sup>145</sup> The essential condition for this reaction appears to be that three halogen atoms must be attached to the  $\beta$ -carbon atom and one or more to the  $\alpha$ -carbon. To illustrate,  $\alpha$ -chloro- $\beta,\beta,\beta$ -tribromodiethyl ether and zinc yield  $\beta,\beta$ -dibromovinyl ether,



while  $\alpha,\beta,\beta,\beta$ -tetrachlorodiethyl ether gives  $\beta,\beta$ -dichlorovinyl ether,



On the other hand, addition of zinc to  $\alpha,\beta,\beta$ -trichloroethyl ether results in the evolution of hydrogen and formation of tarry masses, indicating the elimination of hydrogen chloride by zinc and decomposition of the dichlorovinyl ether formed. When this trichloroether and zinc react in the presence of a large proportion of alcohol, dichloroacetal is the main product.



**Polymerization of Vinyl Ethers.** Ethyl and n-butyl vinyl ethers were almost completely polymerized in 24 hours by 0.2 per cent of iodine, while the  $\beta$ -chloroethyl ether polymerized very slowly and the phenyl compound remained unchanged.<sup>146</sup> The colorless polymers were sticky pitch-like materials, mobile above 100°C., and slowly dissolved in chloroform or benzene. Molecular weight determinations, in the latter solvent, indicated 18-82 units per molecule. When a larger proportion of iodine (0.5 to 5 per cent) was employed, reaction was violent and black polymers, soluble in most of the common solvents (except alcohols), were formed. Methyl, ethyl, and n-butyl vinyl ethers were affected slowly by heat or ultraviolet light, and vigorously by a trace of volatile metallic halides such as stannic chloride or antimony pentachloride.

The rates of polymer formation, at 130°C., of some vinyl ethers are shown in Table 54.

TABLE 54.—Rates of Polymer Formation of Vinyl Ethers.

Ether	Time, Days.	Polymer formed, %.
Vinyl ethyl.....	60	46.5
Vinyl n-butyl.....	60	26.0
Vinyl $\beta$ -chloroethyl.....	3	100.0 (approx.)
Vinyl phenyl.....	90	1.6

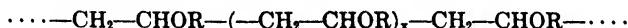
<sup>142</sup> H. S. Hill, *J.A.C.S.*, 1923, 50, 2725.

<sup>144</sup> W. M. Lauer and M. A. Spielman, *J.A.C.S.*, 1931, 53, 1533.

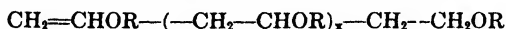
<sup>145</sup> F. Neher and C. L. Fleece, *J.A.C.S.*, 1926, 48, 2416.

<sup>146</sup> W. Chalmers, *Can. J. Research*, 1932, 7, 472; *Brit. Chem. Abs. A*, 1933, 144.

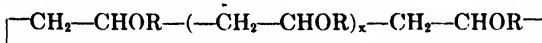
Since polyvinyl ethyl ether yields oxalic acid on oxidation, Chalmers suggests that the structure of this ether, as well as those of its analogues, may be represented by



Whether or not the molecules contain "open" or "ring" structures is difficult to decide. As the polymers gave a small, but measurable, bromine absorption it might be assumed that an ethenoid linkage existed at one end, viz:



Quantitative measurements of bromine absorption, however, did not correspond with the degree of polymerization as indicated by cryoscopic determinations. Hence it appears probable that some polymers may possess a closed structure.



Polymerization of vinyl ethers may be carried out in the presence of compounds (such as vinyl chloride, vinyl acetate, styrene, acrylic nitrile or esters of acrylic or maleic acid) whose essential characteristic is that they contain a double bond in the aliphatic portion of their molecular structure.<sup>147</sup> The products may be employed as linings for apparatus.<sup>148</sup> Reaction may be effected also with the aid of acid-reacting catalysts, e.g., boron fluoride, stannic chloride, aluminum or zinc chloride, sulphuric or hydrochloric acid.<sup>149</sup> Other catalysts include hydrosilicates (Tonsil or Florida earth) or finely divided metals (for example, copper, iron, or nickel) on asbestos or silica gel.<sup>150</sup>

Divinyl ether is polymerized to a black, tarry resin by concentrated sulphuric acid and hydrolyzed rapidly to acetaldehyde by dilute hydrochloric acid. On heating divinyl ether to 70-150°C., using organic peroxides as catalysts, a highly viscous, transparent, resinous material is formed.<sup>151</sup> This latter transformation, however, is inhibited by ammonia.<sup>152</sup> N-Vinyl- $\alpha$ -methyldoline is rapidly transformed into a light yellow resinous mass on keeping.<sup>153</sup>

Vinyl or polyvinyl ethers may be employed in the production of impregnating, polishing, and finishing agents,<sup>154</sup> as components of lacquers,<sup>155</sup> in the preparation of adhesives for laminated glass,<sup>156</sup> as aids in the polymerization of butadiene hydrocarbons by alkali or alkaline earth metals,<sup>157</sup> and as insulating materials.<sup>158</sup> It has been proposed also to add polyvinyl ethers, particularly those from high-molecular-weight ethers, such as the vinyl ether of oleyl or cetyl alcohol, to lubricating oils.<sup>159</sup> Water-resistant films on cellulose esters or ethers may be secured by

<sup>147</sup> French P. 725,844, 1931 and 774,437, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 26, 4827; 1935, 29, 2264. British P. 373,643, 1932; *Chem. Abs.*, 1933, 27, 3788.

<sup>148</sup> British P. 357,173, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4510.

<sup>149</sup> British P. 378,544, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 1071. French P. 734,129, 1932; *Chem. Abs.*, 1933, 27, 1006.

<sup>150</sup> British P. 379,074, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4109.

<sup>151</sup> H. Hibbert, U. S. P. 1,916,423, July 4, 1933; *Brit. Chem. Abs. B*, 1934, 371. Canadian P. 302,437, 1930; *Chem. Abs.*, 1930, 24, 4306.

<sup>152</sup> W. L. Ruigh and R. T. Major, *loc. cit.* C. D. Leake, P. K. Knoefel and A. E. Guedal (*J. Pharmacol.*, 1933, 47, 5; *Chem. Abs.*, 1933, 27, 3252) report that polymerization of divinyl ether is prevented by alkali but hastened by contact with acid.

<sup>153</sup> H. Stach and W. König, *Ber.*, 1930, 63, 88.

<sup>154</sup> British P. 402,512, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3198. French P. 740,097, 1932; *Chem. Abs.*, 1933, 27, 2261.

<sup>155</sup> L. Kollek and H. Ufer, German P. 588,307, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1558.

<sup>156</sup> British P. 368,567, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3576.

<sup>157</sup> G. Ebert, F. A. Fries and P. Garbich, German P. 575,439, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3633.

<sup>158</sup> British P. 408,225, 1934, to H. Rost; *Chem. Abs.*, 1934, 28, 5555.

<sup>159</sup> British P. 413,637, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 592. French P. 761,590, 1934; *Chem. Abs.*, 1934, 28, 4220.

coating with vinyl ether at 0°C. or lower, followed by polymerization of the ether with ultraviolet light at 80-100°C.<sup>100</sup>

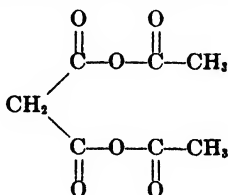
### CHLOROVINYL ARSINES

Acetylene is absorbed by arsenic trichloride, employing aluminum chloride as a catalyst.<sup>101</sup> From the reaction mixture, after treatment with water, three arsenic derivatives may be isolated:  $\beta$ -chlorovinylchloroarsine,  $\text{CHCl}=\text{CHAsCl}_2$ ,  $\beta, \beta'$ -dichlorodivinylchloroarsine,  $(\text{CHCl}=\text{CH})_2\text{AsCl}$ , and  $\beta, \beta', \beta''$ -trichlorodivinylarsine,  $(\text{CHCl}=\text{CH})_3\text{As}$ . From the standpoint of synthetic resins the first of these derivatives is of interest.

Attempts to hydrolyze  $\beta$ -chlorovinylchloroarsine to the corresponding oxide resulted only in the formation of arsenious acid and acetylene. On passing hydrogen sulphide into a carbon tetrachloride solution of the dichloroarsine a thick viscous oil separated. The latter can be dissolved in carbon disulphide and on evaporation of the solvent a pale yellow, viscid liquid of garlic-like odor is obtained. On cooling, this solidified to a hard resin. Analysis indicated it to be  $\beta$ -chlorovinylarsenious sulphide,  $\text{CHCl}=\text{CHAsS}$ . In the preparation of this compound, ethyl alcohol may be substituted for carbon tetrachloride as the solvent for  $\beta$ -chlorovinylchloroarsine.<sup>102</sup>

### CARBON SUBOXIDE

The interest in carbon suboxide ( $\text{C}_3\text{O}_2$ ) from the point of view of synthetic resins lies in its marked tendency to polymerize. The unpolymerized substance is a gas at ordinary temperatures, which can be condensed to a liquid boiling at 7°C. and solidifying at about -110°C.<sup>103</sup> Its chemical properties in many respects are similar to those of a ketene (or diketene). Carbon suboxide unites with water to give malonic acid, with ammonia or amines to furnish amides, and with hydrogen chloride to form malonyl chloride.<sup>104</sup> From the reaction of this oxide with carboxylic acids are obtained mixed acid anhydrides.<sup>105</sup> For example, combination of acetic acid and carbon suboxide apparently gives rise to the compound:



which hydrolyzes to malonic and acetic acids.

The formation of this oxide, and other lower oxides of carbon or polymerized suboxide, was first noted when carbon monoxide was submitted to the action of electrical energy. In view of this fact, a brief discussion of this effect is given before taking up the subject of preparation.

<sup>100</sup> British P. 418,449, 1933, to Celanese Corp. of America; *Brit. Chem. Abs.* B, 1935, 18. See also British P. 418,597, 1933, to Celanese Corp. of America; *Brit. Chem. Abs.* B, 1935, 18.

<sup>101</sup> F. G. Mann and W. J. Pope, *J.C.S.*, 1923, 121, 1754. See also S. J. Green and T. S. Pope, *J.C.S.*, 1931, 119, 448. W. L. Lewis and G. A. Perkins, *Ind. Eng. Chem.*, 1923, 15, 290.

<sup>102</sup> W. L. Lewis and H. W. Stiegler, *J.A.C.S.*, 1925, 47, 2546.

<sup>103</sup> O. Diels and G. Meyerheim (*Ber.*, 1907, 40, 355) give -107°C. to -110°C. as the melting point of the solid. A. Stock and H. Stoltzenberg (*Ber.*, 1917, 50, 489) report -111.3°C. For a discussion of the properties of this oxide, see L. H. Reyeason and K. Kobe, *Chem. Reviews*, 1930, 7, 479.

<sup>104</sup> O. Diels and B. Wolf, *Ber.*, 1906, 39, 699.

<sup>105</sup> O. Diels and L. Lalin, *Ber.*, 1908, 41, 3426.

## ACTION OF ELECTRIC DISCHARGES ON CARBON MONOXIDE

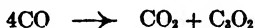
Brodie<sup>106</sup> observed that an electric current effected a contraction in volume of carbon monoxide, and at the same time carbon dioxide and a reddish-brown film (on the sides of the container) were formed. Analysis of the film indicated it to be an oxide of carbon, possibly  $C_2O_3$  or  $C_3O_2$ . He suggested that a series of "oxycarbons" existed, analogous to the acetylene hydrocarbons. Berthelot<sup>107</sup> also obtained the reddish-brown oxide of carbon in a similar manner, but found that heating decomposed the material into carbon monoxide and dioxide, and another oxide to which he assigned the formula  $C_3O_2$ . The latter oxide was secured when carbon monoxide was heated to temperatures of  $500-550^\circ C$ .<sup>108</sup>

Schutzenberg<sup>109</sup> reported that condensation of carbon monoxide by the silent electric discharge ceased as soon as the gas contained 10 per cent carbon dioxide, and that the solid product had the composition  $C_3O_2$ . Furthermore, condensation took place only when the electrodes of the discharge tube were acidulated water (dilute sulphuric acid). Substitution of such electrodes by metallic ones caused the reaction to cease. He therefore considered that the presence of a trace of moisture was essential for the reaction and that water vapor was carried through the glass discharge tube by the current. He later concluded that the water is formed from hydrogen and oxygen (probably generated at the electrodes) which penetrated the glass. Lunt and Mumford,<sup>170</sup> however, found that the type of electrode does not affect the reaction, as carbon monoxide is decomposed readily even when carefully dried. They also believed the brown solid produced by the discharge was not entirely polymerized malonic anhydride ( $C_3O_2$ ) but a mixture probably containing some carbon.

Lunt and Venkataswaran<sup>171</sup> state that decomposition of carbon monoxide can be represented by



and that on removing the solid oxide ( $C_3O_2$ ) from the reaction tube a hydrate,  $C_3O_2 \cdot xH_2O$  ( $x = 1.65$  or  $1.95$ ), is formed. Results obtained by Ott<sup>172</sup> however, indicate that the gases leaving a Siemens ozonizer contain only unimolecular suboxide



and the brown solid remaining is polymerized carbon suboxide.

**Preparation of Carbon Suboxide.** Dehydration of oxygenated organic compounds, particularly esters or acids, serves as a convenient procedure for the preparation of the suboxide. For example, on heating diethylmalonate with a large excess of phosphorus pentoxide to  $300^\circ C$ ., the following reaction occurs,<sup>173</sup>



Other esters of malonic acid (e.g., the dimethyl, dibenzyl, and diphenyl esters) and malonic acid itself also yield the suboxide when treated in a similar manner.<sup>174</sup> Dehalogenation of dibromomalonyl bromide with zinc,<sup>175</sup>

<sup>106</sup> B. C. Brodie, *Proc. Roy. Soc. (London)*, 1873, 21, 245.

<sup>107</sup> M. Berthelot, *Bull. soc. chim.*, 1876, (2), 25, 101; *J.C.S.*, 1876, 30, 596.

<sup>108</sup> M. Berthelot, *Compt. rend.*, 1891, 112, 594; *J.C.S.*, 1891, 60, 901.

<sup>109</sup> P. Schutzenberg, *Compt. rend.*, 1890, 110, 560, 600, 681; 1890, 111, 14; *J.C.S.*, 1890, 58, 691, 692, 1358.

<sup>170</sup> R. W. Lunt and L. S. Mumford, *J.C.S.*, 1929, 1711.

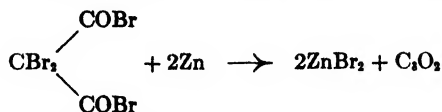
<sup>171</sup> R. W. Lunt and R. Venkataswaran, *J.C.S.*, 1935, 127, 2062; 1927, 857.

<sup>172</sup> E. Ott, *Ber.*, 1925, 58, 772; *J.C.S.*, 1925, 1378.

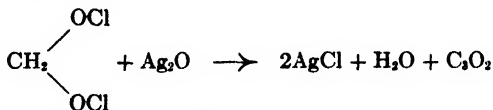
<sup>173</sup> O. Diels and B. Wolf, *Ber.*, 1906, 39, 689.

<sup>174</sup> O. Diels and G. Meyerheim, *Ber.*, 1907, 40, 355. See also A. Stock and H. Stoltzenberg, *Ber.*, 1917, 50, 498.

<sup>175</sup> H. Staudinger and H. Klever, *Ber.*, 1908, 41, 906.

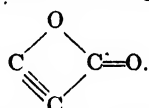


or treatment of malonyl chloride with metallic oxides (silver, lead, or zinc oxide)



are other methods.<sup>176</sup> Ott<sup>177</sup> secured good yields of the suboxide by pyrogenic decomposition of diacetyl tartaric acid or acetoxymaleic acid.

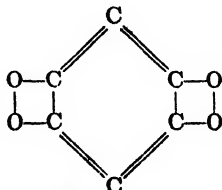
The more generally accepted constitution of carbon suboxide is that proposed by Diels and Wolf<sup>178</sup> who considered the compound to be a diketene having the

formula  $\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$ . Michael<sup>179</sup> suggests a cyclic structure, .

**Polymerization of Carbon Suboxide.** Dry gaseous carbon suboxide is very stable, even at room temperature, when stored in glass containers whose surfaces have not been contaminated with the polymeric form.<sup>180</sup> The presence of mercury or of water vapor, however, effects polymerization of the gas. This reaction is probably a catalytic surface reaction as its velocity cannot be expressed by any simple mathematical formula. Stock and Stoltzenberg<sup>181</sup> believed polymerization of the suboxide to be autocatalytic, the speed depending upon the nature and surface of the containing vessel. They also report that phosphorus pentoxide exerts an accelerating effect.

Liquid carbon suboxide changes within 24 hours to a solid, amorphous, dark red substance which is soluble in water.<sup>182</sup> At 37°C. this polymer loses carbon dioxide and is converted into a material which is only partially soluble. On further heating carbon dioxide, carbon monoxide, and even some carbon suboxide, are evolved and the residue is apparently an oxide of carbon possessing a low oxygen content. Considerable quantities of the polymeric oxide were obtained by Jones and Robinson<sup>183</sup> when they attempted to purify diamyl and diethyl thiomalonates by distillation.

Two structural formulas have been suggested for polymerized carbon suboxide. Hartley<sup>184</sup> gives



<sup>176</sup> H. Staudinger and St. Bereza, *Ber.*, 1908, 41, 4461.

<sup>177</sup> E. Ott, *Ber.*, 1914, 47, 2388; *Umschau*, 1923, 26, 576; *Chem. Abs.*, 1923, 17, 36. E. Ott and K. Schmidt, *Ber.*, 1923, 55, 2136.

<sup>178</sup> O. Diels and B. Wolf, *loc. cit.* See also, O. Diels and G. Meyerheim, *loc. cit.* O. Diels and P. Blumberg, *Ber.*, 1908, 41, 1333.

<sup>179</sup> A. Michael, *Ber.*, 1906, 39, 1915; 1908, 41, 928.

<sup>180</sup> M. J. Edwards and J. W. Williams, *J.C.S.*, 1927, 855.

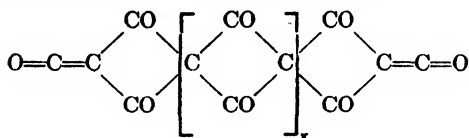
<sup>181</sup> A. Stock and H. Stoltzenberg, *Ber.*, 1917, 50, 493. Cf. E. Ott and K. Schmidt, *Ber.*, 1923, 55, 2136.

<sup>182</sup> O. Diels and B. Wolf, *Ber.*, 1904, 37, 589.

<sup>183</sup> H. O. Jones and C. S. Robinson, *J.C.S.*, 1912, 101, 985.

<sup>184</sup> W. N. Hartley, *Chem. News*, 1906, 94, 49.

and that proposed by Diels, Beckmann and Tonnie<sup>186</sup> is



Carbon suboxide reacts with liquid sulphur dioxide to give an unstable, white, sulphur-containing solid, the first step probably being



followed by polymerization of the latter compound.<sup>188</sup> Malonic acid and the suboxide yield a product resembling polymerized carbon suboxide. Tertiary bases unite with the oxide to form amorphous addition compounds, usually yellow to orange in color, and which are converted into resins on exposure to air. To illustrate, the product with quinine (1 mol of the base to 7 of the oxide) was orange-yellow in color, melted at about 135°C. (with decomposition), and resinified in 3 to 4 days in the air.

Carbon subsulphide, the sulphur analogue of carbon suboxide, can be prepared by conducting the vapors of carbon disulphide through an electric arc<sup>187</sup> or a glass tube heated to 600°C.<sup>188</sup> This sulphide is a liquid having a very disagreeable odor, freezes at -0.5°C., and on being heated to 120°C. changes to a hard black solid. It can be distilled (accompanied by some polymerization) under reduced pressure. Because its chemical properties are analogous to those exhibited by carbon suboxide, Stock and Praetorius<sup>189</sup> believed the constitution of the subsulphide could be represented by  $\text{S}=\text{C}=\text{C}=\text{C}=\text{S}$ .

<sup>186</sup> O. Diels, R. Beckmann and G. Tonnie, *Ann.*, 1924, 439, 76.

<sup>187</sup> O. Diels and K. Hansen, *Ber.*, 1926, 59, 2555.

<sup>188</sup> B. von Lengyel, *Ber.*, 1893, 26, 2960.

<sup>189</sup> H. Aretowski, *Z. anorg. Chem.*, 1895, 8, 314; *J.C.S.*, 1895, 66 (2), 312.

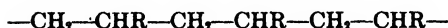
<sup>190</sup> A. Stock and P. Praetorius, *Ber.*, 1912, 45, 3568.

## Chapter 51

# Polyvinyl Esters Polyvinyl Ester Co-Polymers

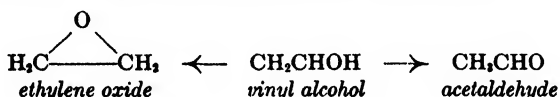
### INTRODUCTION

Esters of the hypothetical vinyl alcohol (e.g., vinyl chloride and vinyl acetate) polymerize to resins which are of particular interest because of their transparency and water-white color. The structure of these polymers may be represented as a long chain-molecule,<sup>1</sup>



in which R represents a halogen atom or an acyloxy group. Also the heteropolymers between the organic and inorganic esters of vinyl alcohol are adhesive and resistant to the action of acids and alkalies and have been suggested as coating agents and as the interlayers of safety glass.

All reactions intended to form vinyl alcohol<sup>2</sup> yield either acetaldehyde or ethylene oxide, both of which are tautomeric with the alcohol:



Vinyl esters, therefore, cannot be made by the usual esterification reaction of treating an alcohol with an acid.<sup>3</sup> Instead, acetylene is used as the source of the alcohol radical. The analogy of vinyl esters to other esters is seen when it is considered that olefins add acids to give saturated compounds, and acetylene unites with acids to yield unsaturated ones. Therefore, since olefins are the dehydration products of saturated alcohols, acetylene may be looked upon as the dehydration product of vinyl alcohol.

Polymers of the inorganic esters of vinyl alcohol, particularly the halides, have been known for many years but the organic esters, typically the acetate, are of more recent discovery. Polymers of the vinyl halides have, however, only limited technical application because of their low solubility and easy thermal decomposition. By employing them mainly in conjunction with organic esters of vinyl alcohol to form co-polymers in which these shortcomings are largely mitigated, plastics of some promise for use in coatings and moldings have been obtained. In this chapter the organic esters will be described first, then the inorganic esters and, finally, co-polymers of the two.

<sup>1</sup> An unsymmetrical combination might be expected also to occur, leading to chains,  $-\text{CH}_2-\text{CHR}-\text{CHR}-\text{CH}_2-\text{CH}_2-\text{CHR}-\text{CHR}-\text{CH}_2-$  or  $-\text{CH}_2-\text{CHR}-\text{CHR}-\text{CH}_2-\text{CHR}-\text{CH}_2-\text{CH}_2-\text{CHR}-$ . The latter, at any rate is ruled out for the polyvinyl halides, since these show microcrystallinity under x-ray examination. An unsymmetrical chain would not be expected to show this. See H. Staudinger, M. Brunner and W. Feisst, *Helv. Chim. Acta*, 1930, 13, 805; *Brit. Chem. Abs. A*, 1930, 1402.

<sup>2</sup> For the influence of potassium hydroxide on the formation of vinyl alcohol from acetaldehyde, see W. L. Evans and C. D. Looker, *J.A.C.S.*, 1921, 43, 1925.

<sup>3</sup> However, it has been reported that acetaldehyde reacts with acetic anhydride in the presence of inorganic acids to give vinyl acetate (G. A. Perkins, *British P.* 418,943, 1933, to Carbide & Carbon Chem. Corp.; *Brit. Chem. Abs. B*, 1935, 56. French P. 767,076. 1934; *Chem. Abs.*, 1935, 29, 177).



## POLYVINYL ORGANIC ESTERS

The most important organic vinyl ester is the acetate. Vinyl chloroacetate also has been studied to some extent, but other esters, such as the propionate, butyrate and trichloroacetate, have received little attention. Vinyl acetate is a mobile, colorless, non-toxic liquid boiling at 73°C.<sup>5</sup> It is formed by the reaction of acetylene and acetic acid in the presence of a catalyst. Many methods for the preparation of this ester have been proposed and the employment of a highly selective catalyst (to minimize secondary reactions) appears to be necessary.

## PRODUCTION OF ORGANIC VINYL ESTERS

When acetylene is passed into glacial acetic acid containing a small quantity of a mercury salt, particularly mercuric sulphate,<sup>6</sup> it is absorbed and converted into esters.<sup>7</sup> If the temperature is kept above about 70°C., ethylidene diacetate is formed to a large extent; at lower temperatures vinyl acetate is obtained, but usually in small proportions. It is probable that vinyl esters are formed first, but unless a low temperature is maintained or they are removed instantly from the reaction mixture, they react further with the acid to give esters of the hypothetical ethylidene glycol. Increased yields of vinyl acetate are secured if acetylene is conducted rapidly through acetic acid (and catalyst) heated to about 70°C.<sup>8</sup> In this manner the acetate is removed (as soon as produced) by the stream of acetylene which is passed through a condenser to recover the ester. Acetylene is recirculated through the catalyst mixture. Boron fluoride alone,<sup>9</sup> or mixed with hydrofluoric acid,<sup>10</sup> has been added to promote reaction in the presence of mercuric oxide. Vinyl butyrate and other esters can be made in a similar manner.<sup>11</sup>

The mercuric sulphate catalyst is more efficient if prepared by dissolving mercuric oxide in acetic acid and adding sulphuric acid, thus precipitating the sulphate in a finely divided state.<sup>12</sup> The catalyst is still more effective if precipitation is accomplished by addition of fuming sulphuric acid, since water formed by the reaction between mercuric oxide and acetic acid is eliminated by combination with sulphur trioxide.<sup>13</sup> A very active catalyst is obtained by treating mer-

<sup>4</sup> A brief description of the production and use of vinyl acetate is given by A. F. Cadenhead, *Chem. Met. Eng.*, 1933, 40, 185; R. Elliot, *Can. Chem. Met.*, 1934, 18, 173.

<sup>5</sup> Other physical constants of vinyl acetate are given by G. O. Morrison and T. P. G. Shaw (*Chem. Met. Eng.*, 1933, 40, 293, and *Trans. Electrochem. Soc.*, 1933, 63, 197; *Brit. Chem. Abs. B*, 1933, 740); J. Marsden and A. C. Cuthbertson (*Can. J. Research*, 1933, 9, 419; *Chem. Abs.*, 1934, 28, 696) and C. Green, J. Marsden and A. C. Cuthbertson (*ibid.*, 1933, 9, 396; *Chem. Abs.*, 1934, 28, 338).

<sup>6</sup> F. Klatte, U. S. P. 1,084,581, Jan. 13, 1914, to Chem. Fabrik Griesheim-Elektron; *Chem. Abs.*, 1914, 8, 991. German P. 271,381, 1912; *Chem. Abs.*, 1915, 9, 356. French P. 461,223, 1913; *Chem. Abs.*, 1914, 8, 3220. British P. 14,346, 1913; *Chem. Abs.*, 1915, 9, 149.

<sup>7</sup> Study of the acetylene-acetic acid reaction was initiated to supply ethylidene diacetate for use as a solvent and as a source of acetic anhydride for the manufacture of cellulose acetate. Since vinyl acetate was always formed as a by-product, it eventually became of interest from the standpoint of the resins which it yielded by polymerisation, and processes were developed which gave this ester as the main product. See G. O. Morrison and T. P. G. Shaw, *loc. cit.*

<sup>8</sup> W. O. Herrmann, H. Deutsch and E. Baum, U. S. P. 1,790,920, Feb. 3, 1931, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 1537. Canadian P. 264,158, 1926; *Chem. Abs.*, 1926, 20, 3696. British P. 231,841, 1925; *J.S.C.I.*, 1925, 44, 942B.

<sup>9</sup> W. Weibezahn, U. S. P. 1,912,608, June 6, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4243. German P. 582,544, 1933; *Chem. Abs.*, 1934, 28, 778.

<sup>10</sup> O. Nicodemus and W. Weibezahn, German P. 604,640, 1934, addn. to 582,544, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 813. French P. 773,476, 1934; *Chem. Abs.*, 1935, 29, 1462.

<sup>11</sup> For the preparation of vinyl trichloroacetate, see H. Walter, U. S. P. 1,669,384, May 8, 1928, to Verein. f. chem. Ind. A.-G.; *Chem. Abs.*, 1928, 22, 2170. British P. 268,707, 1927; *Chem. Abs.*, 1929, 23, 607.

<sup>12</sup> G. Boiteau, British P. 15,919, 1914; *Chem. Abs.*, 1916, 10, 93.

<sup>13</sup> H. W. Matheson and F. W. Skirrow, U. S. P. 1,720,184, July 9, 1929, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1929, 23, 4231. Canadian P. 237,604, 1924; *Chem. Abs.*, 1924, 18, 968. See G. O. Morrison and T. P. G. Shaw (*loc. cit.*) for a further discussion of this catalyst.

curic oxide with a mixture of acetic acid and oleum. In this case the product is the mercury salt of acetylsulphuric acid.<sup>14</sup> With this compound a large yield of vinyl acetate is obtained, amounting to as much as 136 pounds per pound of mercuric oxide employed, provided the temperature of the reaction mixture is kept below 60°C.

Skirrow and Morrison<sup>15</sup> dissolved 20 parts of mercuric oxide in 2000 parts of glacial acetic acid and to this they added, at 85°C., 276 parts of a precipitant formed by dissolving 34 parts of sulphur trioxide in 242 parts of glacial acetic acid at about 20°C. The mixture was cooled to 25°C. and acetylene rapidly passed through it, the temperature gradually rising to about 35°C. The gas and entrained vapors were led through a condenser where vinyl acetate and acetic acid were removed. Acetylene and recovered acid were returned to the reaction zone. After a time the rate of absorption of acetylene slackened owing to reduction of the catalyst. The yield of vinyl acetate was approximately 70 per cent of theoretical based on the acetic acid used and, in this particular instance, amounted to 115 parts of acetate per part of mercuric oxide. If reaction was carried out at 70-100°C. and vinyl acetate returned to the reaction vessel, a high yield of ethylidene diacetate was obtained.<sup>16</sup>

A mixture of mercuric sulphate, sulphoacetic and acetic acid has been proposed as a catalyst.<sup>17</sup> Addition of ferric sulphate is stated to increase the yield of vinyl acetate.<sup>18</sup> Methionic acid,  $\text{CH}_3(\text{SO}_3\text{H})_2$ , and mercury sulphonates dissolved in acetic acid have been suggested also.<sup>19</sup> Zinc and cadmium acetates and benzoates have been used by Reppe<sup>20</sup> to catalyze reaction between acetylene and organic acids. Diluents, both liquid and gaseous, may be employed to reduce danger of explosions.

Skirrow and Morrison<sup>21</sup> found that mercuric orthophosphate is a good catalyst and less tar is formed with it than with mercuric sulphate.<sup>22</sup> One method of preparation consists in dissolving 3 parts of mercuric oxide in 100 parts of glacial acetic acid and adding 2.4 parts of orthophosphoric acid at a temperature of 80-90°C. A stream of acetylene is conducted through the mixture, heated to 78°C. under reflux, until absorption of the gas begins to decrease. On distillation, a total yield of vinyl acetate (including that carried over by the acetylene and re-

<sup>14</sup> A. J. van Peski (*Rec. trav. chim.*, 1921, 50, 103; *Chem. Abs.*, 1921, 15, 3455) reported that sulphur trioxide reacts with acetic acid at ordinary temperatures to give acetylsulphuric acid,  $\text{CH}_3\text{CO}\cdot\text{OSO}_3\text{H}$ , but at high temperatures sulphoacetic acid,  $\text{HSO}_3\text{CH}_2\text{COOH}$ , is formed.

<sup>15</sup> F. W. Skirrow and G. O. Morrison, U. S. P. 1,855,366, Apr. 26, 1932, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1932, 26, 3265. British P. 308,169 and 308,170, 1929; *Brit. Chem. Abs.* B, 1931, 12. German P. 559,436, 1929; *Chem. Abs.*, 1933, 27, 736. Canadian P. 318,838, 1932; *Chem. Abs.*, 1932, 26, 1944.

<sup>16</sup> F. W. Skirrow and G. O. Morrison, U. S. P. 1,855,367, Apr. 26, 1932, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1932, 26, 3265. British P. 335,223, 1929; *Brit. Chem. Abs.* B, 1931, 12. Mercury salts of benzenesulphonic, naphthalenesulphonic or camphorsulphonic acids are not as satisfactory as those of aliphatic sulphonic acids. (German P. 334,554, to Soc. chim. des usines du Rhône; *Chem. Abs.*, 1923, 17, 1801.) Addition of acetic anhydride to a mixture of mercuric sulphate and sulphoacetic acid prevents formation of tars when reaction is carried out at high temperatures to obtain the diacetate. (M. E. Bouvier and L. Hugoniot, U. S. P. 1,680,760, Aug. 14, 1928, to Soc. chim. des usines du Rhône; *Chem. Abs.*, 1928, 22, 3669.) For the use of the mercuric salts of methylene sulphate,  $\beta$ -naphthalenesulphonic acids and sulphoacetic acids in the formation of ethylidene diacetate, see J. Koetschet and M. Beudet, U. S. P. 1,304,959, May 27, 1919, and 1,306,964, June 17, 1919; *Chem. Abs.*, 1919, 13, 2040, 2219.

<sup>17</sup> British P. 351,318, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1932, 26, 5309.

<sup>18</sup> D. E. Strain, U. S. P. 1,849,647, Mar. 13, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 3749. British P. 379,705, 1931; *Brit. Chem. Abs.* B, 1932, 1114.

<sup>19</sup> French P. 770,154, 1934, to Boehringer & Soehne G.m.b.H.; *Chem. Abs.*, 1935, 29, 431.

<sup>20</sup> W. Reppe, German P. 583,332 and 589,970, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1257, 3364. British P. 595,478, 1933; *Chem. Abs.*, 1934, 28, 454. French P. 763,424, 1934; *Chem. Abs.*, 1934, 28, 5469.

<sup>21</sup> F. W. Skirrow and G. O. Morrison, U. S. P. 1,710,197, Apr. 23, 1929, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1929, 23, 3724. Canadian P. 287,494, 1929; *Chem. Abs.*, 1929, 23, 1908.

<sup>22</sup> On the other hand, meta- and pyrophosphates favor high yields of ethylidene diacetates. Mercuric orthophosphate while active gives higher yields of vinyl acetate than the acetylsulphate catalyst, but it becomes inactive sooner so that the yield of ester per pound of mercuric oxide used is less than with the acetylsulphate catalyst. Also it is more expensive. See G. O. Morrison and T. P. G. Shaw, *loc. cit.*

covered) equal to about 95 per cent is obtained. Continuous operation can be effected if fresh catalyst is allowed to run into the reaction vessel before absorption of acetylene starts to slacken and, simultaneously, part of the spent mixture is removed for reactivation.<sup>24</sup>

A vapor-phase process, developed by Baum, Deutsch, Herrmann and Mugdan,<sup>24</sup> consists in passing acetylene and acetic acid vapor through a tube heated to about 200°C. and packed with activated charcoal impregnated with zinc or cadmium acetate. According to Ushakov and Feinstein,<sup>25</sup> the best ratio for the two reactants is 1 part by weight of acid to 9 parts of acetylene. This concentration may be obtained by saturating acetylene with acid vapor at 30°C. From 77 to 84 per cent of the theoretical yield of vinyl acetate resulted. In later investigations, the former workers<sup>26</sup> reported that increasing the rate of flow of the reactants increased the life of the catalyst and the yield of acetate over that of the diacetate. Ushakov and Feinstein noted, however, that a lower yield of vinyl acetate resulted on increasing the rate of flow.

Reaction between acetylene and acetic acid may take place in an inert solvent. Dykstra and Sly<sup>27</sup> passed acetylene into an autoclave containing a mixture of 2400 g. of acetic acid, 328 g. of finely divided mercuric sulphate and 3600 g. of refined kerosene which was stirred and kept at a temperature of 70-75°C. When absorption decreased, the temperature was raised and the rate of flow of acetylene increased. Vinyl acetate (with a sharp boiling range) was obtained by fractionating the distillate. Mugdan and Rost<sup>28</sup> suggest conducting acetylene and acetic acid vapor at 200-300°C. through a suspension of activated carbon and zinc or cadmium salts in a high-boiling hydrocarbon.

Ethylidene diacetate may be used as a source of vinyl acetate. By dissolving about 10 per cent by weight of sulphur dioxide or about 0.4 per cent of syrupy phosphoric acid in the diacetate and heating at 100-170°C., acetaldehyde, acetic anhydride and 15-25 per cent of vinyl acetate are formed.<sup>29</sup>

Vinyl organic esters, which contain hydrophile groups (e.g., hydroxyl, carboxyl and sulphy), have been prepared by heating vinyl chloride with salts of substituted organic acids.<sup>30</sup> Thus, vinyl chloride and monopotassium succinate mixed with toluene and heated in an autoclave at 100-130°C. gave vinyl succinic ester.

#### POLYMERIZATION OF VINYL ACETATE

In the cold, vinyl acetate does not polymerize in the absence of light but, when illuminated, transformation is effected more or less rapidly depending upon the kind of light. When heated to 100°C., or higher, acetate of ordinary purity will

<sup>24</sup> G. O. Morrison, U. S. P. 1,710,181, Apr. 23, 1929, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1929, 23, 2724. Canadian P. 287,495, 1929; *Chem. Abs.*, 1929, 23, 1909.

<sup>25</sup> E. Baum, H. Deutsch, W. O. Herrmann and M. Mugdan, U. S. P. 1,666,482, Apr. 17, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1928, 22, 1983. British P. 182,112, 1922; *J.S.C.I.*, 1922, 42, 861A. German P. 408,784, 1924.

<sup>26</sup> S. N. Ushakov and J. M. Feinstein, *Ind. Eng. Chem.*, 1934, 26, 561.

<sup>27</sup> W. O. Herrmann, H. Deutsch and E. Baum, U. S. P. 1,822,525, Sept. 8, 1931, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 5900. British P. 235,095, 1928; *Brit. Chem. Abs. B.*, 1929, 635. German P. 485,271, 1927; *Chem. Abs.*, 1930, 24, 862. French P. 649,455, 1928; *Chem. Abs.*, 1929, 23, 2986.

<sup>28</sup> H. B. Dykstra and C. Sly, U. S. P. 1,786,647, Dec. 30, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 710. British P. 319,589, 1928; *Chem. Abs.*, 1930, 24, 2470. French P. 653,129, 1929; *Chem. Abs.*, 1930, 24, 4306.

<sup>29</sup> M. Mugdan and T. Rost, German P. 558,071, 1930, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, 26, 4611.

<sup>30</sup> F. W. Skirrow and O. W. Hersberg, U. S. P. 1,538,713, Aug. 9, 1927, to Canadian Electro Products Co., Ltd.; *Brit. Chem. Abs. B.*, 1927, 859. Canadian P. 237,841, 1924, to Shawinigan Laboratories, Inc.; *Chem. Abs.*, 1924, 18, 986.

<sup>31</sup> H. Dreyfus, British P. 398,173, 1933; *Chem. Abs.*, 1934, 28, 1360. See also British P. 385,978, 1932; *Chem. Abs.*, 1933, 27, 4247.

polymerize in the dark and reaction is accelerated by oxygen or peroxides.<sup>31</sup> According to Staudinger and Schwalbach,<sup>32</sup> a trace of oxygen or peroxide is essential for thermal polymerization. A sample of vinyl acetate, distilled in an atmosphere of nitrogen with complete exclusion of oxygen, failed to polymerize when heated at 100°C. in a sealed tube for 6 weeks, but eventually did so when the temperature was raised to 180°C. In the presence of air the same material polymerized at 100°C. in a day.

The influence of oxygen on polymerization is quite different when the reaction mixture (in quartz vessels) is irradiated in the cold with light from a mercury arc. Under these conditions, reaction proceeds more rapidly in the absence of oxygen or in an atmosphere of nitrogen or carbon dioxide.<sup>33</sup> Oxygen, therefore, inhibits photopolymerization of vinyl acetate but accelerates thermal polymerization.<sup>34</sup> On the other hand, oxygen does not retard the photopolymerization of styrene or isoprene.

Although many unsaturated hydrocarbons are polymerized at ordinary temperature by Florida earth, inorganic halides and organic amines, these substances apparently have no influence on vinyl acetate.

#### DEGREE OF POLYMERIZATION OF VINYL ACETATE

Polyvinyl acetate of the highest degree of polymerization has a molecular weight of about 80,000. This material was made by irradiation of the pure ester in an atmosphere of nitrogen and corresponds to a macromolecule containing about 900 monomeric units.<sup>35</sup> Such a resin swells strongly in solvents, is difficult to dissolve and gives solutions of very high viscosity. When heated at 100°C. in the presence of oxygen, vinyl acetate yields a polymer of average molecular weight of about 20,000; with benzoyl peroxide a resin having a molecular weight of about 6000 is obtained.

Polymerization in solution gives, as a rule, products of relatively low molecular weight and reaction is slower. Staudinger and Schwalbach irradiated a chloroform solution of vinyl acetate and, after evaporation of the solvent, the residue (mol. wt. about 3000) was a white, brittle mass which could be powdered easily. Starkweather and Taylor<sup>36</sup> used toluene as a solvent. They believe that the retarding action of the solvent can be ascribed to the activated molecules of the ester giving up their energy to the solvent molecules before combining with other vinyl acetate molecules.

Solvents differ in their inhibiting effect on the reaction and in their influence on the molecular weight of the product. In petroleum ether (b.p. 30-50°C.), transformation occurs rapidly and the molecular weight of the polymer may be as high as 20,000. In this case the polymer is insoluble in the solvent and separates almost as soon as formed. On the other hand, chloroform, chlorobenzene, alcohol, acetone and toluene retard polymerization and give rise to low-molecular weight polymers. With cyclohexanol and cyclohexane as solvents, colored substances are obtained, that from the former being greenish, and from the latter, light red. Polyvinyl acetate obtained by polymerization in chloroform has been shown by Staudinger and Schwalbach to contain chlorine. They assume that hydrogen

<sup>31</sup> F. Klatte and A. Rollett, U. S. P. 1,241,738, Oct. 2, 1917, to Chem. Fabrik. Griesheim-Elektron; *J.A.C.I.*, 1917, 36, 1195. German P. 281,657, 1915 and 281,659, 1914; *J.S.C.I.*, 1915, 34, 628. French P. 474,069, 1914; *J.S.C.I.*, 1915, 34, 724. British P. 15,271, 1915.

<sup>32</sup> H. Staudinger and A. Schwalbach, *Ann.*, 1931, 488, 8.

<sup>33</sup> H. Staudinger and A. Schwalbach, *loc. cit.*

<sup>34</sup> The inhibiting action of oxygen on the photopolymerization of vinyl compounds was observed also by H. S. Taylor and A. A. Vernon, *J.A.C.S.*, 1931, 53, 2527.

<sup>35</sup> H. Staudinger and A. Schwalbach, *loc. cit.*

<sup>36</sup> H. W. Starkweather and G. B. Taylor, *J.A.C.S.*, 1930, 52, 4706.

chloride, resulting from the photochemical decomposition of chloroform, unites with the end valences of the polymer-chains.

Polyvinyl acetate cannot be obtained in a crystalline condition and, according to x-ray evidence, is completely amorphous. In comparison with rubber, it is not elastic. However, polymers having from 150 to 250 vinyl units per molecule are elastic when heated and can be drawn into threads. Under the same conditions, polyacetates containing 30 to 70 vinyl units are not elastic and those having 300 or more units decompose before they soften sufficiently to exhibit elasticity. Unlike rubber, even the stretched polymers show no fiber diagram on x-ray examination.<sup>87</sup> When swollen by treatment with a solvent, polyvinyl acetate does show elastic properties.

While irradiating a benzene solution of vinyl acetate, Staudinger and Schwalbach<sup>88</sup> noticed traces of insoluble, transparent particles on the portion of the quartz tube nearest the light. Insoluble products were obtained also when



Courtesy Plastics Division, Carbide and Carbon Chemicals Corp.

FIG. 131.—A Piece of Vinylite Resin Undergoing Fatigue Test.

vinyl acetate was heated at 180°C. in the presence of oxygen, or at temperatures greater than 200°C. in the absence of oxygen. It was assumed that acetic anhydride was split out between separate chains of the macromolecules thus building up 3-dimensional structures.

#### VARIOUS METHODS OF POLYMERIZATION

One continuous process consists in allowing a vinyl ester to descend a long tube, whose upper part is kept at a temperature just below the boiling point of the liquid by means of cooling devices and whose lower part is maintained at about 200°C. by heating coils. The hot product is ejected at the bottom upon a belt conveyor to cool.<sup>89</sup> Polyvinyl esters, while hot, may be pressed into molds to cool or they may be extruded through nozzles, cooled and disintegrated to form a molding composition.<sup>90</sup>

As previously indicated, vinyl esters polymerize under the influence of heat and light. Klatte and Rollett<sup>91</sup> exposed vinyl acetate and chloroacetate to direct sunlight or to light from a mercury arc, and the esters were eventually converted

<sup>87</sup> G. S. Whitby, J. G. McNally and W. Gally, *Trans. Roy. Soc. Canada*, 1928, 22, 27; *Brit. Chem. Abs. A*, 1928, 1186.

<sup>88</sup> H. Staudinger and A. Schwalbach, *loc. cit.*

<sup>89</sup> British P. 331,692, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 158. French P. 723,460, 1931; *Chem. Abs.*, 1932, 26, 4065.

<sup>90</sup> British P. 333,003 and 333,216, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 76.

<sup>91</sup> F. Klatte and A. Rollett, *loc. cit.*

to solid resins. A shorter exposure to light produced thick syrups which when further exposed in the form of thin layers gave transparent films. Polymerization is accelerated by the addition of oxidizing agents, the most active ones being organic peroxides or ozonides and organic acid anhydrides in conjunction with percarbonates, perborates, silver oxide or other metallic oxides capable of yielding oxygen. Benzoyl peroxide is an efficient catalyst. Incorporation of 0.05-0.1 per cent of this peroxide with vinyl chloroacetate, followed by careful heating, gave a thick syrup in a short time. Polymerization began at 80-100°C. with a rapid rise in temperature, so that the reaction vessel had to be cooled. If the ester was diluted with an indifferent solvent (such as chlorobenzene) the progress of the reaction was moderated. The thick syrup could be further changed to a hard resin by the action of light or by subjecting it to vacuum distillation to remove unpolymerized ester. The final resin could be modified by adding camphor to the ester before treatment.

Schrivver<sup>42</sup> reports acetyl benzoyl peroxide is more active than benzoyl peroxide, since 0.15-0.3 per cent of it (based on the weight of vinyl ester) effected the same degree of polymerization as 1.0 per cent of benzoyl peroxide. Furthermore, the acetyl derivative is more completely used up and is more easily removed from the final product because it is more readily decomposed. Acetyl benzoyl peroxide was made by passing dry air or oxygen through a mixture of benzaldehyde and acetic acid anhydride.

Blaikie<sup>43</sup> prepared similar catalysts by the reaction of aliphatic anhydrides with hydrogen peroxide, sodium peroxide, or true per-salts, i.e., those salts yielding hydrogen peroxide on hydrolysis. A solvent (e.g., vinyl acetate) in which the non-catalytic by-products are insoluble may be employed.

Vinyl resins may be made directly from acetylene without the necessity of isolating the vinyl ester.<sup>44</sup> Acetylene is passed into acetic acid under pressure in the presence of small amounts of metals or metallic compounds such as magnesium, tin or copper; iodine or hydriodic acid; boron compounds or organic acid anhydrides. If acetylene is diluted with an inert gas (nitrogen, benzene or petroleum vapor) the pressure can be increased to 10-15 atmospheres and reaction correspondingly increased without risk of explosion. For example, 26-28 parts of acetylene were gradually passed into a mixture of 50 parts of acetic acid and 1 part of acetic anhydride. The charge was heated at 40-60°C. and the pressure was raised to 5 atmospheres by the introduction of nitrogen. The product consisted of 75 parts of vinyl acetate and 3-5 parts of ethylidene diacetate. If the temperature was then increased to 10 atmospheres or more, the ester was polymerized to bodies which varied in consistency from semi-solids to more or less tough resins.

If vinyl acetate is treated with 0.1 per cent of benzoyl peroxide under pressure and at temperatures up to 100°C. for 2 hours, only 50-60 per cent of the ester is polymerized. The proportion of polymer may be increased (under the same conditions) to about 80 per cent by using the catalyst in the presence of water.<sup>45</sup> The latter also exerts a favorable influence when polymerization is effected in the

<sup>42</sup> L. C. Schriver, U. S. P. 1,333,370, Dec. 12, 1933, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1934, 28, 1360. British P. 397,394, 1933; *Chem. Abs.*, 1934, 28, 780. French P. 748,972, 1933; *Chem. Abs.*, 1933, 27, 5755.

<sup>43</sup> K. G. Blaikie, British P. 337,323 and 337,335, 1933, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1933, 27, 4541.

<sup>44</sup> H. Plauson, U. S. P. 1,425,130, Aug. 8, 1923; *Chem. Abs.*, 1923, 16, 3314. British P. 156,117, 1920, to H. O. Traun's Forschungslab. G.m.b.H.; German P. 372,369, 1918, addn. to 362,750.

<sup>45</sup> W. O. Hermann and E. Baum, U. S. P. 1,536,303, June 1, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; Brit. Chem. Abs. B, 1926, 698. Canadian P. 257,508, 1926; *Chem. Abs.*, 1926, 20, 2333. German P. 431,148 and 430,040, 1924; *Chem. Abs.*, 1930, 24, 2141. Water has also been reported to moderate the violence of the reaction. The later it was added the harder the resin. (French P. 730,348, 1923, to Soc. Nobel française; *Chem. Abs.*, 1934, 28, 915.)

absence of other catalysts. Solutions of hydrogen peroxide, perborates, percarbonates, barium peroxide or calcium peroxide in water are effective and their activity may be enhanced by the addition of alkaline substances such as caustic soda, alkaline phosphates or borates, magnesium or zinc oxide, ammonia or hexamethylenetetramine. For example, 100 parts of vinyl acetate may be heated in an autoclave for 2 hours at 100°C. with (a) 1.5 parts of a 3 per cent solution of hydrogen peroxide, or (b) 0.25 parts of sodium borate and 1.5 parts of 5 per cent hydrogen peroxide solution to form clear masses which, after removal of unpolymerized material by steam distillation, are hard and resin-like. Vinyl butyrate heated with hydrogen peroxide under similar conditions produces a more elastic mass than that from the acetate. Aqueous solutions of partly polymerized vinyl esters may be thickened by treatment with boric acid, a boric ester or hypoborofluoric acid. Gelatinization can be made to take place by this means.<sup>46</sup>

Polymerization of vinyl esters in the presence of catalysts is highly exothermic and often proceeds with almost explosive force. With small batches, one can resort to cooling but this may not be effective on a large scale. Herrmann and Haehnel<sup>47</sup> overcame this difficulty by starting with a small portion of a mixture of vinyl ester and catalyst. This was heated (under reflux) until reaction began, and then the remainder was run in at such a rate that the temperature remained slightly below the boiling point of the ester. At the same time an equal volume of the partly polymerized material was transferred from the reaction vessel to a finishing vessel (also provided with reflux) in which transformation to the polyester was completed. Alcohol may be introduced simultaneously into the finishing vessel and an alcoholic solution of polyvinyl acetate thus formed.

Polymerization in a solvent is slower and more easily controlled and reaction may be stopped before the polymer becomes insoluble in the solvent. For example, equal parts of vinyl acetate and alcohol, together with a small proportion of benzoyl peroxide, may be heated under reflux and a colorless, viscous lacquer of 50 per cent concentration obtained.<sup>48</sup> Blaikie, Morrison and Shaw<sup>49</sup> made polymers of desired softening points and viscosities by regulating the concentration of the unpolymerized vinyl compound present during reaction.

Alcohol containing about 5 per cent of water or turpentine seems to be a better solvent for polyvinyl acetate than alcohol alone.<sup>50</sup> Highly polymerized ester which is insoluble in alcohol may be dispersed in this liquid by first dissolving it in a non-alcoholic solvent, distilling the solution and adding alcohol gradually during distillation until the non-alcoholic solvent has been replaced. An acetic acid solution may be treated in this manner until all the acid has been eliminated. A stiff gel-like paste is formed which can be thinned with more alcohol and used as a lacquer.<sup>51</sup> Addition of a small amount of water to the paste causes it to disperse more easily in alcohol than an unwatered paste.<sup>52</sup>

Another method for effecting polymerization of vinyl compounds in solution consists in heating a portion of the mixture, say 100 g., on a water bath until reac-

<sup>46</sup> A. Voss and W. Starck, German P. 606,440, 1934, to I. G. Farbenind. A.-G.

<sup>47</sup> W. O. Herrmann and H. Haehnel, U. S. P. 1,710,825, Apr. 30, 1929, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1929, 23, 3114. British P. 361,406, 1925; *Chem. Abs.*, 1927, 21, 3369. German P. 490,041, 1925; *Chem. Abs.*, 1930, 24, 2141.

<sup>48</sup> H. Haehnel and W. O. Herrmann, German P. 446,562, 1926, to Consort. f. elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B*, 1929, 28.

<sup>49</sup> K. G. Blaikie, G. O. Morrison and T. P. G. Shaw, British P. 387,353, 1933, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1933, 27, 4540.

<sup>50</sup> W. Haehnel and W. O. Herrmann, German P. 514,435, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 1692.

<sup>51</sup> W. Haehnel and W. O. Herrmann, U. S. P. 1,962,930, June 12, 1934, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 4924. German P. 537,646, 1929; *Chem. Abs.*, 1932, 26, 1404. French P. 707,799, 1930; *Chem. Abs.*, 1932, 26, 861.

<sup>52</sup> H. Haehnel and W. O. Herrmann, German P. 537,531, addn. to 537,646, 1929, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 375.

tion begins and then controlling its course by the gradual addition of the remainder of the solution.<sup>55</sup> For example, a mixture containing 900 g. of vinyl acetate, 600 g. of toluene and 4.5 g. of benzoyl peroxide, treated in this way over a period of about 12 hours, gave an 89 per cent yield of polymer. Butyl acetate, ethyl acetate, benzene, chlorobenzene, ethyl dichloride or methyl ethyl ketone may be used instead of toluene. Di- or trichloroethylene have been suggested also.<sup>56</sup> If di-n-butyl ether is the solvent, the polymer separates as a lower layer and can be dissolved in toluene after decanting the ether. Vinyl chloroacetate gives a somewhat higher yield of polymer by the above procedure than does the acetate. Soluble polymers of vinyl propionate and butyrate can be made also from the corresponding esters in solution, whereas the products formed in the absence of a solvent are usually insoluble. Rushchinskii<sup>57</sup> has suggested the preparation of polyvinyl acetate by heating the monomer in an autoclave in the presence of ether or low-boiling petroleum hydrocarbons.

Lawson<sup>58</sup> recommended the use of an ozone-treated solvent, e.g., methanol through which an ozone-air mixture was passed for 2 hours. Twenty-five g. of vinyl acetate in 44 g. of this liquid, heated for 5 hours under pressure at 90°C., gave a yield of 48 per cent of the polymer. In like manner, chloroacetate showed a 72 per cent conversion.

Application of high pressures increases the velocity of polymerization of vinyl acetate and the rate of reaction approximates one of a first order. It also lowers the temperature at which reaction begins and, under very high pressure, transformation may occur without recourse to heating.<sup>57</sup> Pressures up to 25,000 atmospheres have been suggested.<sup>59</sup>

Polyvinyl esters may contain small proportions of the monomer, acetaldehyde and the acid from which the ester was made. These substances can be removed by steam distillation with subsequent heating (*in vacuo*) of the resin to dry it<sup>60</sup> or by dissolving the resin in a liquid and distilling the solution.<sup>60</sup> Water-soluble material can be eliminated by exposing the resin in a finely divided state (raspings, clippings, threads or thin sheets) to water for several hours.<sup>61</sup> Final traces of acid may be made harmless by adding soluble bases such as diphenylguanidine or phenylhydrazine.<sup>62</sup> Since monomeric vinyl esters are readily hydrolyzed<sup>63</sup> (to acetic acid and acetaldehyde) when heated in acid solution in the presence of mercury compounds, this step can be employed to free the polymer from unpolymerized ester.<sup>64</sup>

<sup>55</sup> W. E. Lawson and L. T. Sanderson, U. S. P. 1,881,282, Oct. 4, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 512; *British P.* 319,590, 1929; *Chem. Abs.*, 1930, 24, 2470. French P. 682,126, 1929; *Chem. Abs.*, 1930, 24, 4306.

<sup>56</sup> W. O. Herrmann and W. Haehnel, U. S. P. 1,976,224, Oct. 9, 1934, to Chem. Forschungs-G.m.b.H.; *Chem. Abs.*, 1934, 28, 7563. The vinyl ester of methoxyacetic acid may be polymerized with benzoyl peroxide, dissolved in dichloromethane and used as a lacquer (German P. 604,776, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 813).

<sup>57</sup> A. L. Rushchinskii, *J. Appl. Chem. (U. S. S. R.)*, 1932, 5, 470; *Chem. Abs.*, 1933, 27, 206.

<sup>58</sup> W. E. Lawson, U. S. P. 1,890,060, Dec. 6, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1939; *British P.* 319,587, 1928; *Chem. Abs.*, 1930, 24, 2470. French P. 682,127, 1929; *Chem. Abs.*, 1930, 24, 4306.

<sup>59</sup> G. Tammann and A. Pape, *Z. anorg. Chem.*, 1931, 200, 113; *Brit. Chem. Abs. A*, 1931, 1239. See also J. B. Conant and C. O. Tongberg, *J.A.C.S.*, 1930, 52, 1659.

<sup>60</sup> *British P.* 365,103, 1930, to Imperial Chem. Ind., Ltd. See also P. W. Bridgman and J. B. Conant, U. S. P. 1,952,116, Mar. 27, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3415. French P. 609,555, 1930; *Chem. Abs.*, 1931, 25, 3358.

<sup>61</sup> *British P.* 305,043, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 4537. French P. 668,490, 1929; *Chem. Abs.*, 1930, 24, 1754.

<sup>62</sup> *British P.* 313,912, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1236.

<sup>63</sup> *British P.* 319,682, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 1015.

<sup>64</sup> G. Kränlein, A. Voss and E. Dickhäuser, German P. 545,441, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 2083. *British P.* 326,287, 1929; *Brit. Chem. Abs. B*, 1931, 73.

<sup>65</sup> For a study of the kinetics of the saponification of vinyl acetate, see A. Skrabal and A. Zahorka, *Monatsh.*, 1927, 48, 459; *Chem. Abs.*, 1928, 22, 344.

<sup>66</sup> C. Steigerwald and R. Zell, German P. 535,348, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 479.



Besides ultraviolet light and the per- compounds mentioned above, other polymerizing agents have been suggested. Taylor<sup>66</sup> subjected a mixture of vinyl acetate and mercury vapors to the resonance radiation of that metal. Young and Douglas<sup>67</sup> added about 2 per cent of lead tetraethyl to vinyl acetate, vinyl chloride, or a blend of the two, and heated the solution for 24 hours in an autoclave at 100°C. Also, a small proportion of acid acts as a catalyst, about 0.5 per cent of hydrochloric acid being sufficient, and the color of the polymer is not adversely affected as when a large quantity of acid is used.<sup>68</sup>

Vinyl esters may be stabilized against polymerization by storage over copper or copper compounds.<sup>69</sup> Sulphur also prevents the esters from forming resins, and only a trace is necessary for this purpose.<sup>69</sup> Such inhibitors are particularly useful if vinyl esters are to be exposed to sunlight.

### COATINGS

Polyvinyl acetate and chloroacetate were early suggested as bases for lacquers, using as solvents, esters, chlorinated hydrocarbons,<sup>70</sup> ketones, aldehydes and nitrohydrocarbons.<sup>71</sup> Since polymerization takes place before the film is formed, there is not as much change with age as is noted with coatings containing drying oils.<sup>72</sup> Other important features of these resins which promote their utilization are light color, flexibility, stability towards light and transparency to ultraviolet rays, and solubility in a wide range of solvents.<sup>73</sup>

Polyvinyl acetate dissolves or swells in polar organic liquids and in some other liquids of a very high dielectric constant.<sup>74</sup> It shows the following behavior in various organic liquids: Hydrocarbons: Insoluble in petroleum hydrocarbons but slowly dissolves in amylene; dissolves in benzene, toluene and xylene, with diminishing readiness. Esters: in general, lower members of a homologous series are better solvents than the higher ones; dissolves very rapidly in methyl and ethyl formates; rapidly, but not quite as fast in methyl and ethyl acetates, less rapidly in  $\beta$ -chloroethyl acetate, ethyl butyrate, benzoate and oxalate; dissolves slowly in butyl oxalate; insoluble in tricresyl phosphate, isoamyl phthalate, ethyl oleate. Ketones: Rapidly dissolves in acetone, less rapidly in methyl ethyl ketone and still less so in ethyl phenyl ketone. Alcohols: Soluble in methyl and ethyl alcohols, swells without dispersing in butyl and amyl alcohols, does not swell in hexyl and heptyl alcohols. Ethers: Swells but does not dissolve in ethyl ether, does not swell in n-butyl ether, dissolves in anisole and, less rapidly, in benzyl ethyl ether, dibenzyl ether and saffrole. Acetals: Methylal is a rapid solvent, but acetal produces only slight swelling. Acids: Dissolves readily in acetic and propionic acids, more slowly in butyric and still more slowly in lactic; insoluble in oleic acid. Aldehydes: Acetaldehyde, propionaldehyde, n-butyraldehyde and valeraldehyde are

<sup>66</sup> H. S. Taylor, U. S. P. 1,746,163, Feb. 4, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 24, 1650.

<sup>67</sup> C. O. Young and S. D. Douglas, U. S. P. 1,775,882, Sept. 16, 1930, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1930, 24, 5308.

<sup>68</sup> French P. 712,303, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 2073.

<sup>69</sup> F. Klatte and A. Zimmermann, German P. 503,919, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5766.

<sup>70</sup> K. G. Blaikie, U. S. P. 1,768,434, June 24, 1930, to Canadian Electro Products Co.; *Brit. Chem. Abs.*, 1931, 621.

<sup>71</sup> Canadian P. 282,800, 1928; *Chem. Abs.*, 1928, 22, 4132.

<sup>72</sup> German P. 290,544, 1913, to Chem. Fabr. Griesheim-Elektron.

<sup>73</sup> German P. 291,299, 1915, addn. to 290,544, to Chem. Fabr. Griesheim-Elektron; *J.S.C.I.*, 1916, 35, 696.

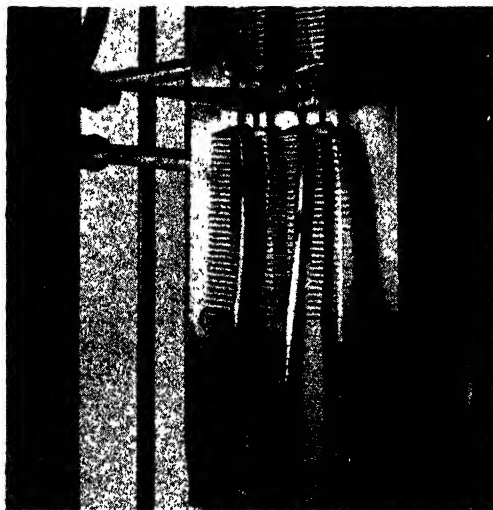
<sup>74</sup> A. Eibner, *Farben-Ztg.*, 1931, 36, 1849, 1892; *Chem. Abs.*, 1931, 25, 5046. H. A. Gardner, *Am. Paint Varnish Mfrs. Assoc. Circ.*, 1928, 337, 637; *Chem. Abs.*, 1929, 23, 292.

<sup>75</sup> Commercial resins of the polymerised vinyl type are on the market under the trade names of Mowlith (I. G. Farbenind. A.-G.), Gelva (Shawinigan Chemicals, Ltd.), and Vinylite (Carbide & Carbon Chem. Corp.). See Fig. 182.

<sup>76</sup> G. S. Whitby, J. G. McNally and W. Galley, *Trans. Roy. Soc. Canada*, 1928 (3), 22 (3), 27; *Brit. Chem. Abs. A*, 1928, 1186.

fairly effective, but benzaldehyde, heptaldehyde, cinnamaldehyde and paraldehyde act very slowly. Halogenated hydrocarbons: Dissolves easily in chloroform and bromoform, less rapidly in propyl chloride and ethyl iodide. Miscellaneous: Dissolves in nitrobenzene and aniline; rapidly in acetonitrile and nitromethane; does not swell in formamide. 1,4-Dioxane<sup>72</sup> is a good solvent.

Colored lacquers are formed by adding dyes, such as water-insoluble amino- or polyamino-anthraquinone dyestuffs, which give colors that are fast to light.<sup>73</sup> The clear, colored products may be used on electric light bulbs.<sup>74</sup> Light-fast enamels contain ultramarine blue, ochre, lampblack or bronze powders.<sup>75</sup> A poly-



Courtesy Plastics Division, Carbide and Carbon Chemicals Corp.

FIG. 132.—Combs of Vinylite Resin Ready to be Automatically Removed as the Two Sides of the Mold Swing Apart.

vinyl acetate solution mixed with red lead is suggested as an anti-rust paint.<sup>76</sup> Better adhesion is obtained with lacquers which are a mixture of polymers of different viscosity characteristics, as for example, high- and low-viscosity polyvinyl acetate or acetate of high viscosity and butyrate of low viscosity.<sup>77</sup> When employed as an undercoat for nitrocellulose lacquers, only a thin film should be applied, as otherwise the top coat tends to crack. A surface coating to render cellophane moisture-proof contains a vinyl polymer with about 1/3 part of paraffin wax and 1/2 part of plasticizer.<sup>78</sup> The solution is applied to sheets of regenerated cellulose and dried by baking.

<sup>72</sup> E. W. Reid and H. E. Hofmann, *Ind. Eng. Chem.*, 1929, 21, 695.

<sup>73</sup> G. Kräusslein, H. Greune and K. Hager, German P. 542,558, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 3130. British P. 334,145, 1929; *Brit. Chem. Abs. B.*, 1930, 1039. French P. 685,925, 1929; *Chem. Abs.*, 1930, 24, 6041. See also French P. 771,901, 1934; *Chem. Abs.*, 1935, 29, 1659. Dye salts formed from sulphonic or carboxylic acid dyes and organic bases, or from basic dyes and acids may be used also. See British P. 350,973, 1933; *Chem. Abs.*, 1933, 26, 3124.

<sup>74</sup> British P. 315,313, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1931, 90.

<sup>75</sup> British P. 350,406, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 3071.

<sup>76</sup> British P. 314,499, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1930, 24, 1537.

<sup>77</sup> British P. 351,768, 1931, to Consort. f. elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B.*, 1933, 235. French P. 713,590, 1931; *Chem. Abs.*, 1933, 26, 3073. W. O. Herrmann and W. Haeckel, U. S. P. 1,964,678, Dec. 18, 1934, to Chemische Forschungs-G.m.b.H.; *Chem. Abs.*, 1935, 29, 943. See also W. Reppe, W. Starck and A. Voss, German P. 593,399, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3255. E. W. Reid, British P. 408,336, 1932, to Carbide & Carbon Chem. Corp.; *Brit. Chem. Abs. B.*, 1934, 371.

<sup>78</sup> W. H. Chace, British P. 330,459, 1931, to Du Pont Cellophane Co., Inc.; *Brit. Chem. Abs. B.*, 1932, 1041.

Polyvinyl acetate is compatible with cellulose nitrate<sup>82</sup> and the methyl, ethyl and benzyl ethers of cellulose, but is not compatible with cellulose acetate. Polyvinyl chloroacetate is compatible only with cellulose ethers. Haehnel and Herrmann<sup>83</sup> found that the addition of polymerized vinyl acetate to nitrocellulose lacquers improves their gloss and adhesion. Flexible lacquers of this type are recommended as coatings for leather.<sup>84</sup> Polyvinyl acetate may be used with cellulose acetate if another synthetic resin compatible with the two is present. Resins for this purpose are those from sulphonamides and formaldehyde, diphenylolpropane and formaldehyde, phenol and furfural, acetone or aniline and furfural, and the resin made by heating lactic acid. Moss<sup>85</sup> made a lacquer by dissolving 100 parts of vinyl acetate resin, 30 parts of diphenylolpropane-formaldehyde resin and 30 parts of cellulose acetate in 300 parts of acetone.

Plauson<sup>86</sup> suggested the preparation of colloidal solutions of the suspensoid type from polymerized vinyl esters and an organic non-solvent, the mixture of resin and liquid being passed through a colloid mill. The resin may also be finely divided and dispersed in water.<sup>87</sup> The dispersion was applied by spraying and, after drying, the film was baked. Emulsions which could be used as coating compositions were formed when a solution of polyvinyl acetate in an organic solvent was added to water containing a protective colloid.<sup>88</sup>

An ink applicable to intaglio printing has been made by dissolving 50 parts of polyvinyl acetate in a mixture of 10 parts of cyclohexanone, 10 parts of ethyl acetate and 30 parts of alcohol, and incorporating a pigment consisting of 7.5 parts of lampblack and 2.5 parts of the calcium salt of the azo-dyestuff prepared from aniline and 2,6-naphtholsulphonic acid.<sup>89</sup> Before use the ink is diluted with alcohol. The composition is applied either by relief or lithographic printing. A viscous solution of vinyl compound has been employed as a binder for metal powders used in color printing.<sup>90</sup>

Solutions of vinyl resins may be used for coating wall paper, tapestries,<sup>91</sup> or fabrics,<sup>92</sup> for the impregnation of cloth to form shoe-stiffeners,<sup>93</sup> and for the sizing of yarns of viscose or other cellulose esters.<sup>94</sup> Scouring of the tightly twisted sized yarn with a solvent produces a crepe effect.<sup>95</sup> Vinyl esters have been employed for a combined impregnating and cementing of layers of fibrous material. In this manner sheets which are impervious to gases have been made and suggested

<sup>82</sup> H. E. Hofmann, *Ind. Eng. Chem.*, 1931, 23, 127.

<sup>83</sup> W. Haehnel and W. O. Herrmann, German P. 559,402, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 887.

<sup>84</sup> O. Dorr and M. Hofmann, British P. 369,260, 1930; *Brit. Chem. Abs. B*, 1932, 475. French P. 705,219, 1930, to Soc. Dorr & Hofmann; *Chem. Abs.*, 1931, 25, 5309.

<sup>85</sup> W. H. Moss, U. S. P. 1,902,257, Mar. 21, 1933, to Celanese Corp. of America; *Chem. Abs.*, 1933, 27, 3350. British P. 345,521, 1930, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1931, 597. Canadian P. 318,768, 1932, to C. Dreyfus; *Chem. Abs.*, 1932, 26, 2052.

<sup>86</sup> H. Plauson, U. S. P. 1,436,820, Nov. 28, 1922; *Chem. Abs.*, 1923, 17, 642. British P. 156,149, 1920, to H. O. Traun's Forschungslab. G.m.b.H.; *J.S.C.I.*, 1922, 41, 381A.

<sup>87</sup> H. Scheidemann, German P. 527,445, 1930, to A. Wacker Ges. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 4725. British P. 372,385, 1931; *Brit. Chem. Abs. B*, 1932, 737.

<sup>88</sup> German P. 549,073, 1930, to I. G. Farbenind. A.-G. and Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, 26, 3943. For the inclusion of water-soluble cellulose ethers, see British P. 308,284, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 239.

<sup>89</sup> H. Fleischmann and O. Jordan, U. S. P. 1,737,239, Dec. 30, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 833. British P. 307,877, 1929; *Brit. Chem. Abs. B*, 1930, 26. French P. 671,082, 1929; *Chem. Abs.*, 1930, 24, 1996.

<sup>90</sup> French P. 774,851, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2265.

<sup>91</sup> British P. 344,118, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4725.

<sup>92</sup> W. H. Moss, British P. 372,327, 1930, to British Celanese Ltd.; *Chem. Abs.*, 1933, 27, 3047.

<sup>93</sup> W. O. Herrmann and W. Haehnel, U. S. P. 1,523,526, Sept. 8, 1931, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 3959. See also R. B. Frasier, U. S. P. 1,979,461, Nov. 6, 1934, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1935, 29, 257.

<sup>94</sup> H. Dreyfus and W. I. Taylor, British P. 346,267, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1932, 26, 2066.

<sup>95</sup> H. Dreyfus, British P. 352,451, 1930; *Brit. Chem. Abs. B*, 1931, 880.

for use in gas masks.<sup>96</sup> Tissue paper coated with a vinyl acetate enamel has been advocated for cigarette tips.<sup>97</sup> A method of making articles impermeable to liquids is to condense on their cold surfaces the vapors of unpolymerized acetate, which is then polymerized by means of light, heat or catalysts (benzoyl peroxide).<sup>98</sup>

### ADHESIVES

An adhesive for joining various surfaces consists of a mixture of polymerized vinyl ester and isobutyl phthalate dissolved in methyl alcohol.<sup>99</sup> Polyvinyl acetate has been recommended for securing abrasive materials to steel discs.<sup>100</sup> It may be used also for making composite sheets from thin foils of cellulose derivatives.<sup>101</sup> Müller and Stelkens<sup>102</sup> prepared a powdered, dry glue containing polyvinyl acetate, ethylacetanilide and cellulose acetate or ethyl cellulose. A liquid adhesive is made up from 40 parts vinyl ester resin, 4-12 parts cellulose ester and 60 parts of a volatile solvent.<sup>103</sup>

Shatter-proof or safety glass consists of a sandwich layer of a tough plastic cemented between glass plates. Being colorless, transparent to both visible and ultraviolet light, non-yellowing, resistant to cold and possessing good adherence to glass, the vinyl resins show promise in this field. In most instances, however, their toughness is not sufficient to warrant using them without a layer of cellulose nitrate or acetate to impart the necessary strength.<sup>104</sup> Thus, a solution of polyvinyl acetate (in alcohol or ethyl acetate) may be employed for cementing glass sheets with films of cellulose derivatives.<sup>105</sup> Polyvinyl butyrate may be substituted for the acetate.<sup>106</sup> The layer of cellulose derivative may consist of cellulose acetate plasticized by a tartaric ester<sup>107</sup> or triacetin.<sup>108</sup> In this case adhesion is improved by mixing some of the plasticizer with the vinyl resin cement.<sup>109</sup>

When cellulose nitrate serves as the strengthening layer, there is a tendency to yellowing in sunlight. Bresser<sup>110</sup> observed that this defect may be diminished by using a mixture of cellulose nitrate and vinyl resin. Other cellulose derivatives which have been suggested for use in conjunction with polyvinyl esters in safety glass include the light-fast, fatty acid esters and mixed esters, e.g., the laurates, naphthenates and acetate-butyrate and butyrate-laurate mixtures.<sup>111</sup>

In another proposed form of safety glass, the layer of cellulose derivative is omitted and only a layer of vinyl resin placed between the sheets of glass. A

<sup>96</sup> British P. 373,947, 1931, to Röhm & Haas A.-G.; *Brit. Chem. Abs. B*, 1932, 722. French P. 728,640, 1931; *Chem. Abs.*, 1932, 26, 6035.

<sup>97</sup> British P. 363,676, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1726. See also W. Becker, German P. 516,710, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3139.

<sup>98</sup> British P. 418,449, 1934, to Celanese Corp.; *Chem. Abs.*, 1935, 29, 2266.

<sup>99</sup> W. O. Herrmann and W. Haeckel, U. S. P. 1,784,003, Dec. 9, 1930, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 389. British P. 271,090, 1927; *Brit. Chem. Abs. B*, 1928, 793. French P. 694,186, 1927; *Chem. Abs.*, 1928, 22, 3748. Canadian P. 277,169, 1928; *Chem. Abs.*, 1928, 22, 2644. *Cf. M. Sakuma*, Japanese P. 101,052, 1933; *Chem. Abs.*, 1934, 28, 4849.

<sup>100</sup> C. Krug, German P. 545,004, 1929; *Chem. Abs.*, 1932, 26, 3081.

<sup>101</sup> British P. 334,280, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1933, 27, 353.

<sup>102</sup> R. Müller and W. Stelkens, French P. 701,353, 1930; *Chem. Abs.*, 1931, 25, 4097. W. Stelkens, British P. 361,317, 1930; *Chem. Abs.*, 1933, 27, 1116.

<sup>103</sup> E. L. Kallander and G. R. Alden, Canadian P. 345,324, 1934, to Dennison Mfg. Co.; *Chem. Abs.*, 1935, 29, 2363.

<sup>104</sup> *Chem. Age (London)*, 1932, 27, 472. See also W. Huth, *Farben-Chem.*, 1932, 3, 427, 465; *Chem. Abs.*, 1933, 27, 1826. *Plastic Products*, 1934, 10, 131. C. H. Zefer, *Glashütte*, 1933, 63, 319, 321, 340, 563; *Chem. Abs.*, 1933, 27, 5913.

<sup>105</sup> British P. 314,379, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1930, 24, 1477. French P. 678,399, 1929; *Chem. Abs.*, 1930, 24, 2352.

<sup>106</sup> French P. 690,751, 1930, to Soc. des usines chim. Rhône-Poulenc; *Chem. Abs.*, 1931, 25, 1351.

<sup>107</sup> British P. 335,678, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 1963.

<sup>108</sup> W. H. Moss, U. S. P. 1,831,462, Nov. 10, 1931, to Celanese Corp. of America; *Chem. Abs.*, 1932, 26, 632. British P. 341,891, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1931, 255.

<sup>109</sup> French P. 633,564, 1929, to Soc. des usines chim. Rhône-Poulenc; *Chem. Abs.*, 1929, 23, 5291.

<sup>110</sup> A. Bresser, *Chem. Appl.*, 1932, 19, 62; *Chem. Abs.*, 1932, 26, 4929.

<sup>111</sup> British P. 315,667, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 320. *Cf. F. Meyer*, British P. 404,263, 1933; *Brit. Chem. Abs. B*, 1934, 236. French P. 727,043, 1933; *Chem. Abs.*, 1933, 27, 1471.

plasticizer<sup>118</sup> is mixed with the resin and the plastic applied either as a viscous solution or as a powder, followed by heating the composite under pressure.<sup>118</sup> The condensation product obtained by heating maleic anhydride with castor oil or 1,3-butylene glycol, when mixed with polyvinyl acetate, increases its adhesion to glass and renders it more resistant to cold.<sup>114</sup> The co-polymer of vinyl acetate and acrylate may be substituted for polyvinyl acetate.<sup>118</sup> These various types of plastics can be made to flow between heated sheets of glass by forcing them through fine copper tubes.<sup>116</sup> Walsh and Caprio<sup>117</sup> introduced vinyl acetate between glass plates and subjected the composite to pressure, thus forming the resin *in situ*. Wilson<sup>118</sup> suggested that a plasticizing agent, dibutyl phthalate, be employed as the strengthening layer.

In general, adhesives derived from vinyl acetate (also the methyl and ethyl esters of acrylic acid) may be utilized for gluing metal to metal, glass to glass, and textiles to leather. The bond is said to be flexible, durable, and resistant to water and to many organic solvents.<sup>119</sup>

### MOLDED PRODUCTS

When polyvinyl esters are heated to at least 100°C. in the presence of acid catalysts (lactic, hydrochloric or acetic acid or the chlorides of zinc or aluminum) the resulting products are elastic and more or less infusible and insoluble. If no catalysts are used the temperature must be raised to 200°C. Vinyl resins may therefore be employed to make buttons, umbrella handles, gears and other articles.<sup>120</sup> Objects are said to have been formed by spraying a concentrated solution of polyvinyl ester into a mold and allowing it to harden.<sup>121</sup> The method of injection molding has also been employed.<sup>122</sup>

Sheaths of polyvinyl acetate have been suggested as electrical insulators.<sup>123</sup> Rost<sup>124</sup> produced electrical cables by coating wires with layers of vinyl resins. Besides polyvinyl acetate, the substances resulting from the action of aldehydes on polyvinyl compounds<sup>125</sup> can be used. Dickie and Stafford<sup>126</sup> have described the preparation of films or sheets from the polyesters.

Medvedev<sup>127</sup> reported that the addition of polyvinyl acetate (up to 20 per cent) to cellulose nitrate films increased resistance to elongation. Rigidity, on the

<sup>118</sup> As a plasticizer 5-25 per cent of camphor may be used with dibutyl phthalate. A. Renfrew and J. S. B. Fleming, British P. 403,723, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 3549. French P. 788,994, 1934; *Chem. Abs.*, 1934, 28, 3204.

<sup>119</sup> British P. 349,283, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 580. French P. 695,330, 1930; *Chem. Abs.*, 1931, 25, 2927. See also A. Renfrew, British P. 393,855, 1932, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1934, 97. J. G. Davidson, U. S. P. 1,929,352, Oct. 3, 1933, to Carbide & Carbon Chem. Corp.; *Chem. Abs.*, 1934, 28, 277.

<sup>120</sup> G. Kränlein, A. Voss and E. Diekhäuser, German P. 547,384, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3633. British P. 367,658, 1931, addn. to 349,283, 1929; *Brit. Chem. Abs. B*, 1932, 423. See also British P. 372,579, 1932, addn. to 363,933, 1930; *Chem. Abs.*, 1933, 27, 3575.

<sup>121</sup> British P. 368,567, 1931, addn. to 349,283, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 507. French P. 40,116, 1931, addn. to 695,330, 1930; *Chem. Abs.*, 1933, 27, 824.

<sup>122</sup> British P. 384,153, 1932, to Consort. f. elektrochem. Ind.; *Brit. Chem. Abs. B*, 1933, 106.

<sup>123</sup> J. F. Walsh and A. F. Caprio, U. S. P. 1,835,619, Dec. 8, 1931, to Celluloid Corp.; *Chem. Abs.*, 1932, 26, 1086.

<sup>124</sup> J. Wilson, British P. 389,106, 1933, to Triplex Safety Glass Co., Ltd.; *Chem. Abs.*, 1933, 27, 5920.

<sup>125</sup> F. Ohl, *Gelatine, Leim, Klebstoffe*, 1934, 2, 147; *Chem. Abs.*, 1934, 28, 7437. See also L. V. D. Soorah and J. Wilson, British P. 421,897, 1933, to Triplex Safety Glass Co., Ltd.; *Brit. Chem. Abs. B*, 1933, 198.

<sup>126</sup> British P. 323,157, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 111.

<sup>127</sup> F. Posner, German P. 540,552, 1929, to Deutsche Legrit G.m.b.H., C. Lindstrom, W. Letzel & Co.; *Chem. Abs.*, 1932, 26, 2600.

<sup>128</sup> F. Posner, German P. 557,636, 1931, addn. to 540,552, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 617.

<sup>129</sup> H. Rost, British P. 393,418, 1933; *Chem. Abs.*, 1933, 27, 5447.

<sup>130</sup> H. Rost, British P. 407,718, 1934; *Chem. Abs.*, 1934, 28, 5556.

<sup>131</sup> See Chapter 62.

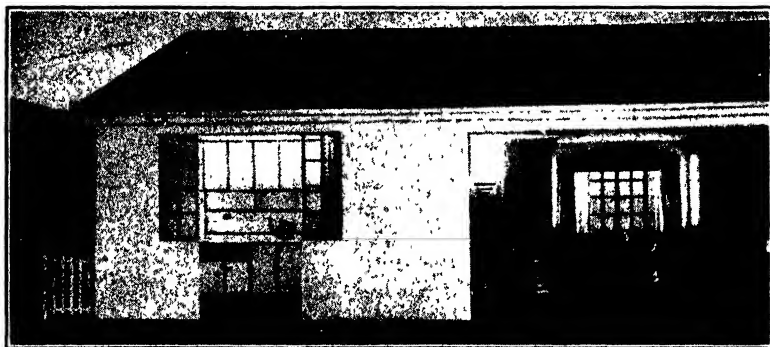
<sup>132</sup> W. A. Dickie and C. E. Stafford, British P. 405,002, 1934, to British Celanese, Ltd.; *Chem. Abs.*, 1934, 28, 4905.

<sup>133</sup> A. I. Medvedev, *J. Appl. Chem. (U. S. S. R.)*, 1933, 6, 880, 889; *Brit. Chem. Abs. B*, 1934, 56.

other hand, decreased. The presence of 10 per cent of this acetate improved the mechanical properties of denitrated cellulose nitrate.

Vinyl resins mixed with dispersions of rubber yield gutta-percha-like compositions<sup>120</sup> or with ground slate, cork and wood flour furnish linoleum substitutes or artificial leather.<sup>120</sup> About 10 per cent of vinyl acetate polymer in a rubber composition is asserted to give a vulcanized product that is resistant to gasoline.<sup>120</sup> Molding compositions have been made from vinyl resins and cellulose ethers<sup>121</sup> or esters.<sup>122</sup> Sound records are prepared from mixtures of polyvinyl acetate esters<sup>123</sup> and amorphous silica.<sup>124</sup> Products for this use are procured also by blending monomeric vinyl compounds and waxes and polymerizing the former *in situ*.<sup>125</sup>

Frank<sup>126</sup> suggested the formation of artificial silk threads by spinning solutions of cellulose esters or ethers and polyvinyl acetate. Rayon of improved softness, suppleness and increased resistance to water is obtained from cellulose xanthate and the xanthate of polyvinyl alcohol.<sup>127</sup> Dreyfus<sup>128</sup> employed mixtures of two vinyl acetate polymers having different viscosities. An artificial fabric is also made



Courtesy Carbide and Carbon Chemicals Corporation

Fig. 133.—Display Rooms Fabricated Almost Entirely of Vinylite Resins.

by impregnating wood pulp with a solution of polymerized vinyl ester in butyl acetate and then drying.<sup>129</sup>

Davidson and McClure<sup>130</sup> have described the commercial molding and many uses of vinyl resins. Among the various molded forms made possible by the low

<sup>120</sup> A. E. Murphy, British P. 373,263, 1932, to Dunlop Rubber Co., Ltd., and Anode Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 3854.

<sup>121</sup> Dörr & Hofman, British P. 313,578, 1928, to Consort. f. elektrochem. Ind. G.m.b.H. and O. Dörr; *Chem. Abs.*, 1930, 24, 1189. O. Dörr, French P. 676,544, 1929, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1930, 24, 3092. British P. 406,367, 1934, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 5190.

<sup>122</sup> M. C. Reed, Canadian P. 346,163, 1934, to Carbide & Carbon Chem. Corp.; *Chem. Abs.*, 1935, 29, 2260.

<sup>123</sup> British P. 308,658, 1929, to Celluloid Corp.; *Brit. Chem. Abs. B*, 1930, 1146.

<sup>124</sup> British P. 355,533, 1929, to Celluloid Corp.; *Brit. Chem. Abs. B*, 1930, 1146.

<sup>125</sup> British P. 368,621, 1931, to Consort. f. elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs.*, 1932, 475. See also W. O. Herrmann, U. S. P. 1,963,030, Dec. 4, 1934, to Chemische Forschungs-G.m.b.H.; *Chem. Abs.*, 1935, 29, 526.

<sup>126</sup> J. E. Symonds, U. S. P. 1,946,597, Feb. 13, 1934, to United Research Corp.; *Chem. Abs.*, 1934, 28, 2481.

<sup>127</sup> French P. 769,707, 1934, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1935, 29, 526. British P. 429,564, 1934; *Brit. Chem. Abs. B*, 1935, 161.

<sup>128</sup> G. Frank, British P. 311,784, 1928, to Röhm & Haas A.-G., and R. O. Herzog; *Chem. Abs.*, 1930, 24, 963.

<sup>129</sup> British P. 365,982, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1755. French P. 720,618, 1931; *Chem. Abs.*, 1932, 26, 3920.

<sup>130</sup> H. Dreyfus, British P. 399,171, 1933; *Chem. Abs.*, 1934, 28, 1803.

<sup>131</sup> W. E. Lawson, U. S. P. 1,959,983, Apr. 3, 1934, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1935, 185.

<sup>132</sup> J. G. Davidson and H. B. McClure, *Ind. Eng. Chem.*, 1933, 25, 645.

shrinkage of these resins are wall panels and doors, both of which are molded around a fibrous core.

It is stated that the addition of polymerized fatty-acid vinyl esters, e.g., the acetate or stearate, to lubricating oils and greases improves their properties.<sup>141</sup> Alternatively, the monomer may be added to the hydrocarbon and polymerization effected *in situ* with boron fluoride. Oils thus treated have a lower cold test and a higher viscosity index.

#### MODIFIED ORGANIC-ESTER RESINS

The properties of vinyl resins may be modified either by treatment, for example with sulphur chloride to effect vulcanization,<sup>142</sup> or by incorporation of other materials during or after resinification. Thus, vinyl resins may be milled with rubber and the mixture vulcanized,<sup>143</sup> or lampblack incorporated with partially polymerized vinyl acetate before milling.<sup>144</sup> Rubber and vinyl compounds, heated under pressure, in the presence of a hydrocarbon solvent and sulphur and a heavy-metal chloride, yield a light-colored solution which may be employed as a lacquer.<sup>145</sup> Vinyl ester may be polymerized in a liquid medium (aliphatic hydrocarbon or alcohol) containing an emulsifying agent,<sup>146</sup> e.g., a cellulose derivative.

Plauson<sup>147</sup> made a complex resin (which was tougher than a straight phenol-formaldehyde resin) by heating 94 parts of phenol, 28-30 parts of paraformaldehyde and 86 parts of vinyl acetate in a closed vessel at 70-120°C. Unreacted ingredients were removed afterwards by heating at 100°C. under reduced pressure. Alternatively, phenol and formaldehyde may be combined first and the resulting resin heated with vinyl acetate under pressure. Reaction can be effected also in the presence of a solvent.

Vinyl esters condense with phenols when catalysts (hydrochloric or phosphoric acid, ferric, aluminum or zinc chloride) are employed.<sup>148</sup> Heating the condensate, with or without sulphur, causes it to harden. Fatty oils or long-chain fatty acids, factice or cellulose esters may be added prior to condensation. Vinyl esters can also be partially polymerized before condensation with phenols.<sup>149</sup> Niederl, Smith and McGreal<sup>150</sup> have studied the reaction between phenol and vinyl acetate in the presence of concentrated sulphuric acid. The product was an amorphous solid, a polymer of o-vinyl-phenol. It was assumed that phenoxyglycol acetate, first formed, is hydrolyzed and that the resulting glycol is dehydrated by the acid to phenyl vinyl ether which undergoes rearrangement to give o-vinyl-phenol. The latter compound is then polymerized by the acid. Phenyl acetate is also formed from phenol and vinyl acetate.<sup>151</sup>

<sup>141</sup> British P. 413,637, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1934, 1001. See also French P. 761,530, 1934; *Chem. Abs.*, 1934, 28, 4220.

<sup>142</sup> W. O. Herrmann and W. Haehnel, U. S. P. 1,672,157, June 5, 1928, to Consort. f. elektrochem. Ind.; *Chem. Abs.*, 1928, 22, 2686. Canadian P. 271,571, 1927; *Chem. Abs.*, 1927, 21, 3767.

<sup>143</sup> British P. 353,194, 1930, to Soc. des usines chim. Rhône-Poulenc; *Chem. Abs.*, 1932, 26, 5452.

<sup>144</sup> British P. 328,812, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5538.

<sup>145</sup> British P. 378,900, 1931, to Röhm & Haas A.-G.; *Brit. Chem. Abs. B*, 1932, 997. See also French P. 717,087, 1931, to Radiochemische Forschungs-Institut G.m.b.H.; *Chem. Abs.*, 1932, 27, 1217.

<sup>146</sup> French P. 765,363, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6956.

<sup>147</sup> H. Plauson, U. S. P. 1,451,843, Apr. 17, 1923; *Chem. Abs.*, 1923, 17, 2058. German P. 364,045, 1918, to Plauson's Forschungs-Institut G.m.b.H. British P. 156,151, 1920, to H. O. Traun's Forschungslab. G.m.b.H.; *J.S.C.I.*, 1922, 41, 381A. Canadian P. 226,633, 1922; *Chem. Abs.*, 1923, 17, 1157.

<sup>148</sup> British P. 333,166, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 610. French P. 675,668, 1929; *Chem. Abs.*, 1930, 24, 3758.

<sup>149</sup> French P. 38,160, 1930, addn. to 675,668, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 5525.

<sup>150</sup> J. B. Niederl, R. A. Smith and M. E. McGreal, *J.A.C.S.*, 1931, 53, 3930.

<sup>151</sup> When phenols or alcohols are heated with vinyl esters in the presence of acid catalysts the vinyl group is replaced forming a new ester and acetaldehyde (H. Deutsch and W. O. Herrmann, British P. 314,646, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B*, 1929, 708. French P. 653,705, 1928; *Chem. Abs.*, 1929, 23, 3713. German P. 578,378, 1933; *Chem. Abs.*, 1933, 27, 4248. Cf. W. Langenbeck and J. Baltes, *Ber.*, 1934, 67, 687; *Brit. Chem. Abs. A*, 1934, 509). If vinyl esters are passed at a high temperature through a reaction vessel packed with wood charcoal on which zinc oxide has been

Aldehyde<sup>188</sup> resins such as those obtained by treating acetaldehyde with sodium hydroxide may be combined with polymerized vinyl compounds by fusing the two together. These composite resins may be used for molding or as shellac substitutes.<sup>189</sup> It has also been proposed to mix urea-formaldehyde resins with vinyl resins to form a molding composition.<sup>184</sup>

Rosin and polyvinyl acetate, although not compatible, may be combined by heating to about 250°C.<sup>186</sup> The resin thus formed is soluble in benzene and linseed oil but insoluble in alcohol or alkalis. It probably consists, at least partially, of a polyvinyl ester of rosin as a result of the elimination of acetic acid. Linseed oil heated with a mixture of rosin and the polyacetate yields a varnish. Other acids (stearic, ricinoleic or naphthenic) and manila copal may be substituted for rosin. Replacement of the acetate group by other radicals (e.g., lactate, tartrate or citrate) may be effected by refluxing polyvinyl acetate with the appropriate acid.<sup>186</sup>

Polyvinyl compounds which are soluble or dispersible in water were prepared by Dreyfus<sup>187</sup> by the partial hydrolysis of the corresponding polyester. The partially hydrolyzed esters may be condensed with aldehydes to increase their resistance to wear and to weathering.<sup>188</sup> The water absorption of such resins is low and consequently resistance to humidity is improved. Lacquers prepared from them are somewhat similar to those from nitrocellulose in respect to toughness, are harder and more durable, and have an advantage over oil varnishes because of their greater speed of drying. The modified resins are soluble in a wide range of solvents including solvent naphtha mixed with alcohol, methyl and ethyl alcohol, acetone, dioxane, ethylene glycol monoethyl ether, ethyl acetate, chloroform and dichloroethylene.

Voss<sup>189</sup> made plastic substances, having a low solubility in water and organic solvents, by heating vinyl esters to about 150°C. in the presence of condensing agents, such as zinc chloride or hydrogen chloride. Robertson<sup>190</sup> reduced the fusi-

deposited, ketene, various ketones, acetaldehyde, acid anhydrides and vinyl ethers are produced. (H. Deutsch and W. O. Herrmann, German P. 515,807, 1927, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 1537.) Acetic anhydride in a yield of about 77 per cent is obtained by boiling vinyl acetate under reflux with acetic acid and a little sulphuric acid (W. O. Herrmann and H. Deutsch, U. S. P. 1,856,251, May 3, 1932, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, 26, 3820, British P. 288,549, 1928; *Brit. Chem. Abs. B*, 1929, 122.) If water is included in the mixture, the vinyl acetate decomposes to give acetic acid and acetaldehyde. (H. Deutsch and W. O. Herrmann, German P. 555,234, 1927, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, 26, 5103.) By heating vinyl acetate with acetic acid in the presence of fuming sulphuric acid or a mercury compound, a yield of 85-90 per cent of the theoretical amount of ethylidene diacetate may be obtained. (F. W. Skirrow and J. Dick, U. S. P. 1,449,918, Mar. 27, 1923; *Chem. Abs.*, 1923, 17, 2290, Canadian P. 228,127, 1923; *Chem. Abs.*, 1923, 17, 1241.) Ethylidene diacetate yields decomposition products similar to those obtained from vinyl acetate. For example, ethylidene diacetate heated with monosodium phosphate or metaboric acid in an inert solvent, forms acetic anhydride and acetaldehyde (J. Koetschet and M. Beudet, U. S. P. 1,398,356, March 25, 1919; *Chem. Abs.*, 1919, 13, 1715) and heated with concentrated sulphuric acid it produces acetic anhydride and paraldehyde. (J. Koetschet and M. Beudet, U. S. P. 1,306,963, June 17, 1919; *Chem. Abs.*, 1919, 13, 2219.) If instead of adding the sulphuric acid directly, kieselguhr is saturated with it and then added, the side reactions are minimized and a high yield of pure acetaldehyde and acetic anhydride is obtained (H. Deutsch, German P. 391,874, 1921, addn. to 365,079, 1919, to Consort. f. elektrochem. Ind. G.m.b.H.; *J.S.C.I.*, 1924, 43, 811B).

<sup>182</sup> For various aldehyde-modified vinyl resins, see Chapter 52.

<sup>183</sup> H. Deutsch, W. O. Herrmann and W. Haehnel, German P. 534,936, 1923, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, 26, 1143, British P. 314,399, 1929; *Brit. Chem. Abs. B*, 1930, 872. See also W. O. Herrmann, H. Deutsch and W. Haehnel, U. S. P. 1,985,993, Jan. 1, 1935, to Chemische Forschung-G.m.b.H.; *Chem. Abs.*, 1935, 29, 1176.

<sup>184</sup> British P. 309,487, 1928, to Kunstharzfabrik F. Pollak Ges.; *Chem. Abs.*, 1930, 24, 740.

<sup>185</sup> A. Voss, German P. 506,143, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 389.

<sup>186</sup> H. Dreyfus, British P. 335,973, 1933; *Chem. Abs.*, 1933, 27, 4247.

<sup>187</sup> H. Dreyfus, British P. 336,005, 1933; *Chem. Abs.*, 1933, 27, 4247.

<sup>188</sup> F. W. Skirrow and S. Whyte, British P. 405,986, 1933; *Brit. Chem. Abs. B*, 1934, 371. See also F. W. Skirrow, G. O. Morrison and K. G. Blaikie, British P. 351,083, 1930, to Canadian Electro Products Co.; *Brit. Chem. Abs. B*, 1931, 553. Cf. D. T. Jones, A. Renfrew and B. Burns, British P. 404,279, 1932, to Imperial Chem. Ind. Ltd.; *Brit. Chem. Abs. B*, 1934, 244. D. T. Jones and A. Renfrew, British P. 407,060, 1933, to Imperial Chem. Ind. Ltd.; *Brit. Chem. Abs. B*, 1934, 414.

<sup>189</sup> A. Voss, German P. 575,996, 1933, addn. to 536,497, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1590. French P. 656,161, 1923; *Chem. Abs.*, 1930, 24, 1595.

<sup>190</sup> F. Robertson, U. S. P. 1,921,326, Aug. 8, 1932, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1933, 27, 4263.



bility and solubility of polymerized vinyl esters by precipitating the resin in an alkaline solution. For example, 500 parts of an acetone solution containing 250 parts of vinyl resin were added slowly to 250 parts of a mixture of ethyl and isopropyl alcohols (equal parts by volume) containing 1 per cent of caustic soda. The mixture was stirred vigorously and 500 parts of water were added. The precipitated resin was filtered, washed with water and dried.

To remove air from compact masses of vinyl acetate resin, Renfrew<sup>161</sup> covered the block with a hydrocarbon oil and heated in an autoclave to 60°C. under a pressure of 400 lb. per square inch. The pressure was not released until the temperature had fallen to 20°C. (12 hours). Dreyfus<sup>162</sup> reported that incorporation of alkylolamines,  $\omega$ -aminoalkylamides of fatty acids or partially esterified polyhydric alcohols rendered the manufacture and manipulation of films of polyvinyl resins less difficult.

A mixed resin usable in lacquers is made by polymerizing a vinyl compound in the presence of an arylsulphonamide-aldehyde resin.<sup>163</sup> When polyvinyl esters are polymerized in liquids of the extracted stand-oil type, resins are obtained whose solutions serve as quick-drying lacquers. Oils employed in making such compositions are prepared by treating partially polymerized drying oils with solvents, for example, the higher alcohols or esters such as ethyl malonate,<sup>164</sup> which remove the nonpolymerized portion leaving the highly polymerized residue.<sup>165</sup> Further addition of oil or cellulose derivatives to the vinyl-oil condensate can be made.<sup>166</sup>

The product from polyvinyl esters and stand-oil extract is known as Olovine.<sup>167</sup> This forms hard, colorless, water-resistant films of high gloss, which are difficult to saponify and which do not turn yellow on aging. Cobalt salts accelerate their drying. Olovine in butyl acetate can be used with nitrocellulose as a lacquer.<sup>168</sup> Mixed with fibrous fillers it can be employed for phonograph records.<sup>169</sup>

Lawson and Sandborn<sup>170</sup> mixed vinyl compounds with nonpolymerized drying oils and then polymerized the composition in the absence of water. Heuck,<sup>171</sup> on the other hand, recommended using emulsions of unsaturated oils in water. Rosin and rosin esters can be added to the vinyl esters prior to polymerizing.<sup>172</sup> Plauson<sup>173</sup> made rubber-containing lacquers by heating rubber, vinyl acetate, acetic acid and trinitrophenol with a volatile hydrocarbon solvent. The addition of 5 per cent of a polyvinyl ester to chlorinated rubber is said to give a varnish base.<sup>174</sup>

Vinyl acetate, emulsified in a 10 per cent casein solution and irradiated with

<sup>161</sup> A. Renfrew, British P. 398,194, 1932, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 1558.

<sup>162</sup> H. Dreyfus, British P. 387,710, 1933; *Chem. Abs.*, 1933, 27, 4672.

<sup>163</sup> French P. 721,717, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4190.

<sup>164</sup> A. Eibner, W. O. Herrmann, W. Haehnel and M. Miller, U. S. P. 1,984,297, Nov. 7, 1932, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 483. A. Eibner, German P. 549,151, 1930, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, 26, 3633. British P. 367,102, 1930; *Brit. Chem. Abs.* B, 1932, 487. French P. 708,408, 1930; *Chem. Abs.*, 1932, 26, 1142.

<sup>165</sup> Such oils are called Tekalol. See Chapter 61.

<sup>166</sup> A. Eibner, W. O. Herrmann, W. Haehnel and M. Miller, U. S. P. 1,956,551, May 1, 1934, to Consort. f. elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs.* B, 1935, 194. French P. 718,689, 1931; *Chem. Abs.*, 1932, 26, 3392. German P. 573,208, 1930; *Chem. Abs.*, 1933, 27, 3093.

<sup>167</sup> A. Eibner, *Farben-Ztg.*, 1931, 37, 13, 54, 88; *Chem. Abs.*, 1932, 26, 606.

<sup>168</sup> T. H. Barry and L. Light, *British Plastics, Synth. Appl. Finishes*, 1932, 3, 3, 23; *Brit. Chem. Abs.* B, 1933, 806.

<sup>169</sup> British P. 406,367, 1932, to Consort. f. elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs.* B, 1934, 371. See also French P. 741,924, 1933; *Chem. Abs.*, 1933, 27, 3628.

<sup>170</sup> W. E. Lawson and L. T. Sandborn, British P. 392,924, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 353.

<sup>171</sup> C. Heuck, German P. 563,202, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1217. French P. 747,583, 1933; *Chem. Abs.*, 1933, 27, 5203.

<sup>172</sup> H. J. Barrett, U. S. P. 1,942,531, Jan. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1717.

<sup>173</sup> H. Plauson, U. S. P. 1,900,693, March 7, 1933, to Radiochem. Forschungs-Institut G.m.b.H.; *Chem. Abs.*, 1933, 27, 3094.

<sup>174</sup> G. Schultze, U. S. P. 1,980,980, Nov. 12, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 530.

light from a mercury arc, yields a vulcanizable product approaching rubber in elasticity.<sup>176</sup> A similar result is obtained if the protein be suspended in vinyl acetate with the addition of benzoyl peroxide and heated. Emulsions of mixtures of butadiene and vinyl compounds<sup>176</sup> may also be polymerized to rubber-like substances.<sup>177</sup>

Resins from vinyl chloroacetate are susceptible to modification by replacement of the chlorine. For example, treated with pyridine, polyvinyl chloroacetate yields a polyvinylammonium base which is soluble in water and useful in dyeing.<sup>178</sup> Polyvinyl chloroacetate also reacts with the alkali compounds of organic acids, phenols or alcohols, in a liquid which is a solvent for the polymer, to give pale-colored, chlorine-free resins. Sodium salts of drying oil acids, potassium phenolate, sodium glyceroxide or sodium butyl phthalate, used in this way, furnish a variety of resin types.<sup>179</sup>

Vinyl esters are capable of undergoing heteropolymerization by reaction with maleic anhydride and other  $\alpha,\beta$ -unsaturated acids. Voss and Dickhäuser<sup>180</sup> slowly heated a mixture of 86 parts of vinyl acetate, 50 parts of maleic anhydride and 0.6 parts of benzoyl peroxide under reflux. They obtained a light-colored, transparent resin in the form of a hard block which could be pulverized. The resin is soluble in acetone and in aqueous alkali solutions but is insoluble in alcohol and in benzene and thus differs from unmodified vinyl resin. A mixture of equal parts of styrene, vinyl acetate and maleic anhydride in acetone, heated in the same way, gives (after distilling off the solvent) a colorless, homogeneous, tough block which can be turned or planed. These heteropolymers may be hydrolyzed to water-soluble products. Morrell and Samuel<sup>181</sup> report that maleic anhydride and vinyl acetate do not react in the absence of a catalyst. Aqueous solutions of polyvinyl acetate-maleic acid polymers are recommended for the sizing and dressing of textiles<sup>182</sup> and they may be used in the preparation of color lakes<sup>183</sup> and of aqueous dispersions of dyestuffs and sulphur.<sup>184</sup> The polymers may be further treated with compounds such as glycerol capable of reacting with the anhydride groups.<sup>185</sup> Thus treated, the resins are insoluble in alkalies. Another heteropolymer is formed by heating vinyl acetate and trichloroethylene with a small quantity of benzoyl peroxide. This chlorine-containing polymer is a viscous liquid which hardens at ordinary temperatures.<sup>186</sup> Some of the trichloroethylene enters the reaction; the remainder acts as a solvent for the polymerized ester.

<sup>176</sup> W. Frankenburger and C. Steigerwald, U. S. P. 1,756,943, May 6, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 3399. German P. 544,325, 1927; *Chem. Abs.*, 1932, 26, 2622. British P. 294,474, 1928; *Brit. Chem. Abs. B*, 1929, 1024. French P. 656,049, 1928; *Chem. Abs.*, 1929, 23, 4102.

<sup>177</sup> The vinyl esters may be replaced by styrene. See Chapter 11.

<sup>178</sup> British P. 364,089, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 494.

<sup>179</sup> A. Voss, W. Schumacher and C. E. Müller, German P. 542,778, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3387.

<sup>180</sup> H. B. Dykstra and W. E. Lawson, U. S. P. 1,975,087, Oct. 2, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 7564. British P. 364,400, 1931; *Chem. Abs.*, 1933, 27, 1775.

<sup>181</sup> A. Voss and E. Dickhäuser, German P. 540,101, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1818. British P. 376,479, 1931; *Brit. Chem. Abs. B*, 1932, 948. French P. 719,145, 1931.

<sup>182</sup> R. S. Morrell and H. Samuel, *J.C.S.*, 1932, 2215.

<sup>183</sup> A. Voss, K. Joachim, E. Dickhäuser and H. Geier, German P. 553,174, 1930, and 571,665, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4724; 1933, 27, 4419. French P. 728,712, 1931; *Chem. Abs.*, 1932, 26, 6160.

<sup>184</sup> British P. 359,643, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 427.

<sup>185</sup> British P. 369,915, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 764. French P. 717,906, 1931; *Chem. Abs.*, 1932, 26, 2875.

<sup>186</sup> A. Voss and E. Dickhäuser, German P. 544,326, 1930, addn. to 540,101, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2609. British P. 376,481, 1931, addn. to 376,479, 1931; *Brit. Chem. Abs. B*, 1932, 948.

<sup>187</sup> W. O. Herrmann and W. Haehnel, U. S. P. 1,976,224, Oct. 9, 1934, to Chem. Forschungs G.m.b.H.; *Chem. Abs.*, 1934, 28, 7563. German P. 550,833, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1932, 26, 4925. The production of plastic masses, applicable either as molding materials or ingredients for lacquers, from fibers of polyvinyl alcohol and polyvinyl acetate (soluble in alcohol) is described by W. O. Herrmann and W. Haehnel, U. S. P. 1,996,744, Apr. 23, 1935, to Chem. Forschungs G.m.b.H.

## POLYVINYL INORGANIC ESTERS

In comparison with the organic polyvinyl esters, the polymers of the inorganic esters have a lower degree of solubility and are much less stable when heated. Acetylene is the basic material from which the monomers are prepared, although ethylene addition products, for example, ethylene dichloride, may also be used.

## PREPARATION OF VINYL HALIDES

Vinyl halides are most conveniently prepared from the dihalogen-substituted ethanes. Vinyl chloride is obtained by treating ethylene dichloride with alcoholic potash<sup>187</sup> or with potassium hydroxide dissolved in methanol.<sup>188</sup> Ethylidene dichloride and sodium ethylate may also be used.<sup>189</sup> Dropped slowly into a saturated alcoholic solution of potassium hydroxide heated under reflux on a water bath, ethylidene dichloride begins reacting at about 35°C. (ethylene dichloride needs a slightly higher temperature). The reaction goes on slowly without further heating, producing a continuous evolution of vinyl chloride.<sup>190</sup> Vinyl chloride may be obtained by passing ethylene dichloride or ethylidene dichloride over hot contact masses such as pumice,<sup>191</sup> alumina<sup>192</sup> or active charcoal.<sup>193</sup> Using the last catalyst and ethylene dichloride a temperature of 230-350°C. was satisfactory. Both acetylene and vinyl chloride are formed by heating ethylene dichloride to 800°C., or a lower temperature in the presence of steam.<sup>194</sup> The production of acetylene, rather than of vinyl chloride, is favored by the presence of diluents, reduced pressure or increase in time of heating. Trichloroethane when treated with zinc, aluminum or iron at 50-120°C. in the presence of water or steam<sup>195</sup> produces vinyl chloride.

Acetylene and gaseous hydrogen chloride react at 180°C. in the presence of metallic chlorides to yield vinyl chloride.<sup>196</sup> Mercuric chloride on silica gel is an especially active catalyst, forming vinyl chloride even at 25°C.<sup>197</sup> Herrmann and Baum<sup>198</sup> used metal halides of the second and fifth groups (barium and bismuth chlorides) supported on activated silica gel. At 160-200°C., activated carbon itself is a catalyst.<sup>199</sup>

<sup>187</sup> Regnault, *Ann.*, 1835, 14, 28, 34. Cf. Swiss P. 159,148, 1933, to Escher Wyss Maschinenfabriken A.-G.; *Chem. Abs.*, 1933, 27, 4543, for the preparation of vinyl bromide from coke-oven gas.

<sup>188</sup> British P. 349,263, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5312. French P. 694,575, 1930; *Chem. Abs.*, 1931, 25, 5312.

<sup>189</sup> Wurtz and Frapolli, *Ann.*, 1858, 108, 224. Cf. J. Spence (*J.A.C.S.*, 1933, 55, 1290) for the preparation of vinyl iodide from 1,2-diiodoethane.

<sup>190</sup> J. A. Nieuwland and (Sr.) M. Florentine, paper delivered at Detroit (Mich.) meeting, American Chemical Society, Sept. 7, 1927.

<sup>191</sup> H. Bilts, *Ber.*, 1902, 35, 3524; *J.C.S.*, 1903, 84 (1), 1.

<sup>192</sup> J. B. Senderens, *Compt. rend.*, 1908, 146, 1213; *Chem. Zentr.*, 1908, 2, 227.

<sup>193</sup> German P. 588,793, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1361.

<sup>194</sup> J. P. Baxter, W. A. M. Edwards and R. M. Winter, U. S. P. 1,986,876, Jan. 8, 1935, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 1099. British P. 363,009, 1930; *Chem. Abs.*, 1933, 27, 1345. German P. 596,256, 1934; *Chem. Abs.*, 1934, 28, 4436. French P. 721,808, 1931; *Chem. Abs.*, 1933, 26, 4067.

<sup>195</sup> German P. 525,309, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4012. British P. 353,842, 1929; *Chem. Abs.*, 1932, 26, 5312.

<sup>196</sup> German P. 278,249, 1912, to Chem. Fabrik. Griesheim-Elektron; *Chem. Abs.*, 1915, 9, 1096. French P. 462,711, 1913; *J.S.C.I.*, 1914, 33, 277. British P. 21,134, 1913; *J.S.C.I.*, 1915, 34, 818. These processes also include the use of the catalyst in solution or suspension. German P. 288,584, 1913, addn. to 278,249, 1912; *Chem. Abs.*, 1916, 10, 3502.

<sup>197</sup> J. P. Wibaut and J. van Dalfsen, *Rec. trav. chim.*, 1932, 51, 626; *Chem. Abs.*, 1932, 26, 4580.

<sup>198</sup> W. O. Herrmann and E. Baum, U. S. P. 1,919,886, July 25, 1933, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 4315.

<sup>199</sup> F. K. Fertsch, U. S. P. 1,933,894, April 18, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3224.

Vinyl chloride is also formed by the reaction of hydrogen chloride on nascent acetylene. Plauson<sup>200</sup> treated calcium carbide with concentrated hydrochloric acid at 60-95°C. in the presence of a catalyst (a mixture of a mercury and a copper salt). Reaction occurs without a catalyst if the pressure is increased above atmospheric, although some of the vinyl halide is polymerized under these conditions. Vinyl chloride distills off as it is formed; and, if a stream of hydrogen chloride



*Courtesy Plastics Division, Carbide and Carbon Chemicals Corp.*

FIG. 134.—Extrusion of Vinylite Plastic.

is passed through the reaction mixture during the operation, the yield is almost quantitative. Small quantities of zinc, aluminum or tin chlorides accelerate the addition of hydrogen chloride to give vinyl chloride, but ferric chloride accelerates formation of dichloroacetaldehyde, which is normally present in small amounts as a by-product.

Ostromislensky<sup>201</sup> passed purified acetylene through a 10 per cent solution of hydrochloric acid containing mercuric chloride and obtained vinyl chloride. Ac-

<sup>200</sup> H. Plauson, U. S. P. 1,445,168, Feb. 12, 1923; *Chem. Abs.*, 1923, 17, 1481. Canadian P. 227,823, 1923; *Chem. Abs.*, 1923, 17, 1241. British P. 154,120, 1920, to H. O. Traun's Forschungslaboratorium G.m.b.H.; *J.S.C.I.*, 1923, 41, 437A.

<sup>201</sup> I. Ostromislensky, U. S. P. 1,541,174, June 9, 1925, to Naugatuck Chem. Co.; *Chem. Abs.*, 1925, 19, 2210.

cording to Nieuwland and Foohey,<sup>202</sup> vinyl chloride is formed when acetylene is conducted into a solution containing cuprous chloride and ammonium chloride and saturated with hydrogen chloride. If both cuprous and cupric chlorides are present, an equilibrium mixture of cis- and trans-dichloroethylene is formed. Cupric chloride solutions do not absorb acetylene in the absence of cuprous chloride. Perkins<sup>203</sup> prepared vinyl chloride by passing acetylene at 65°C. through an aqueous solution containing about 12 per cent of hydrogen chloride and about 40 per cent of catalyst. The latter consisted of equal amounts of cuprous chloride and calcium chloride. Additional hydrogen chloride was supplied to maintain the concentration, and vinyl chloride was isolated from the issuing gaseous mixture. Toussaint<sup>204</sup> made vinyl chloride from acetylene and hydrogen chloride using mercuric chloride dissolved in anhydrous stannic chloride as a catalyst.

Acetylene reacts with hydrogen bromide to form vinyl bromide.<sup>205</sup> An 80 per cent yield can be obtained by treating a mixture containing 1.5 parts of acetylene and 1 part of hydrogen bromide by volume with actinic rays at 0°C.<sup>206</sup>

According to Plauson,<sup>207</sup> the addition of hydrogen halides to acetylene hydrocarbons takes place smoothly and rapidly at 100-120°C. under a pressure of 1-2 atmospheres. By increasing the pressure and raising the temperature when all the acetylene has reacted, polymerized products may be obtained without the necessity of isolating the intermediate halides.

#### POLYMERIZATION OF VINYL CHLORIDE

Vinyl chloride<sup>208</sup> and bromide<sup>209</sup> polymerize readily on standing and rapidly under the influence of light. The chloride, exposed to sunlight, forms under the conditions of treatment an amorphous, insoluble body having a specific gravity of 1.406, and melting with decomposition above 130°C.<sup>210</sup> If exposure to light is not too long, the polymer is soluble in chlorobenzene and the solution can be used as a lacquer. Films of the material are transparent, tough and noninflammable. Softened by mastication with chlorobenzene, it can be pressed and used as a celluloid substitute.<sup>211</sup>

According to Guyer and Schütze,<sup>212</sup> vinyl bromide is not polymerized by nitric acid or by some metals such as copper or zinc. Some polymerization was effected by lead dioxide, nickelic oxide on diatomaceous earth, and aluminum or iron and zinc foil. Hydrogen peroxide was apparently the most effective agent. Iron and bronze surfaces inhibited polymerization.

Plotnikow<sup>213</sup> observed that solutions of vinyl chloride in ethyl alcohol, acetone, carbon tetrachloride, methyl alcohol, ether, and toluene, when exposed to the action of ultraviolet light at temperatures of 15-25°C., deposited a white powder. In the

<sup>202</sup> J. A. Nieuwland and W. L. Foohey, *Proc. Indiana Acad. Sci.*, 1929, 38, 196; *Chem. Abs.*, 1931, 25, 2633.

<sup>203</sup> G. A. Perkins, U. S. P. 1,934,324, Nov. 7, 1933, to Carbide & Carbon Chem. Corp.; *Chem. Abs.*, 1934, 28, 488. Canadian P. 329,042, 1933, to Carbide & Carbon Chem. Corp.; *Chem. Abs.*, 1933, 27, 1865.

<sup>204</sup> W. J. Toussaint, U. S. P. 1,926,638, Sept. 12, 1933, to Carbon & Carbide Chem. Corp.; *Chem. Abs.*, 1933, 27, 5756.

<sup>205</sup> Reboul, *Jahresber.*, 1872, 304.

<sup>206</sup> W. Bauer, U. S. P. 1,414,852, May 2, 1922; *Chem. Abs.*, 1922, 16, 2150.

<sup>207</sup> H. Plauson, U. S. P. 1,425,130, Aug. 8, 1922; *Chem. Abs.*, 1922, 16, 3314; British P. 156,117, 1920, to Traun's Forschungslaboratorium G.m.b.H.; *J.S.C.I.*, 1922, 41, 436A. German P. 373,369, 1918, addn. to 362,750.

<sup>208</sup> Vinyl chloride is a gas at ordinary temperatures; its boiling point is -13.9°C. For other physical constants, see L. I. Dana, J. N. Burdick and A. C. Jenkins, *J.A.C.S.*, 1927, 49, 2301.

<sup>209</sup> Vinyl bromide boils at 16°C. under 750 mm. pressure. See R. Anschütz, *Ann.*, 1883, 221, 141; *J.C.S.*, 1884, 46, 33.

<sup>210</sup> E. Baumann, *Ann.*, 1872, 163, 217; *Chem. Zentr.*, 1873, 23.

<sup>211</sup> Germau P. 281,877, 1913, to Chem. Fabrik Griesheim-Elektron; *J.S.C.I.*, 1915, 34, 623.

<sup>212</sup> A. Guyer and H. Schütze, *Helv. Chim. Acta*, 1934, 17, 1544; *Chem. Abs.*, 1935, 29, 1771.

<sup>213</sup> J. Plotnikow, *Z. wiss. Phot.*, 1922, 21, 117; *J.S.C.I.*, 1922, 41, 361A.

presence of salts of manganese, cobalt, nickel, copper, vanadium and uranium, reaction was catalyzed and took place in visible light.<sup>224</sup> Uranyl salts in sunlight were quite effective. The product resembled rice powder and was slightly soluble in acetone, methyl and ethyl alcohol, more soluble in benzene, carbon tetrachloride and carbon bisulphide, and very soluble in phenyl acetate. From those solvents in which it was fairly soluble, the polymer was recovered as an elastic film which lost its elasticity on keeping. When mixed with 40 per cent of French turpentine, 40 per cent of cedar oil, 65 per cent of pine oil or 60 per cent of camphor, yellow masses were obtained. Thirty per cent of castor oil converted it into a somewhat sticky, light gray mass, and with 60 per cent of copaiba balsam it yielded a dark wax-like mixture. With 70-75 per cent of castor oil or 75 per cent of pine oil, a vaseline-like mass was obtained. Jellies were produced on mixing with 50-70 per cent of aniline or 65-70 per cent of tetralin (tetrahydronaphthalene); while with 40 per cent of tetralin, 50 per cent of Peru balsam or 23 per cent of rosemary oil, it gave a solid, elastic mass. Flumiani<sup>225</sup> regarded the gels formed by polyvinyl chloride as relatively simple in comparison with such substances as gelatin and agar. He also found that the product from photopolymerization in the presence of uranyl nitrate was miscible with nitrobenzene, acetophenone, phenanthrene and naphthalene, giving solutions of varying degrees of dispersion.<sup>226</sup>

Ostromislensky<sup>227</sup> isolated what he considered to be several different types of polyvinyl chloride based on their solubility. The first of these ( $\alpha$ -polymer) is soluble in acetone and in chlorobenzene and is formed by the action of ultraviolet light in the presence of a catalyst (such as a soluble lead salt). If polymerization is continued, the product ( $\beta$ -polymer) is insoluble in acetone although still soluble in chlorobenzene. Further polymerization results in an insoluble body ( $\gamma$ -polymer), but if the reaction is interrupted just before the stage of complete insolubility is reached, the material will swell when treated with strong solvents ( $\delta$ -polymer). The  $\beta$ -polymer yields transparent films which remain flexible much longer than films of the  $\alpha$ -polymer. They may be plasticized by dichlorobenzene, chloronaphthalene, naphthalene, diphenylmethane, acetophenone, o-chlorophenol, benzyl chloride, ethyl benzoate, glycol diacetate or anisole. In the polymerization<sup>228</sup> of vinyl chloride by ultraviolet light, any  $\alpha$ -modification which has not been entirely converted into the  $\beta$ -form may be removed by extracting it with acetone. The  $\beta$ -polymer can also be obtained from the  $\gamma$ - or  $\delta$ -forms by heating them with aniline, quinoline, nitrobenzene or benzophenone. When polymerization is carried out in solution, the formation of insoluble material is retarded and is prevented almost entirely if chlorobenzene, ether, alcohol or tetrachloroethane are used as solvents.

Lawson and Werntz<sup>229</sup> produced the  $\alpha$ -polymer of vinyl chloride by heating the unpolymerized chloride at 90-120°C. in a solvent and in the presence of a catalyst such as benzoyl peroxide, ozone or barium peroxide. The solvents proposed were ethylene dichloride, methyl alcohol, chlorobenzene and ethyl acetate. It was suggested that this polymer be used for molding and as a coating. If, in addition to benzoyl peroxide, trioxymethylene is employed to catalyze the reaction, the  $\gamma$ -form is obtained.<sup>230</sup> Tetrahydrofurfuryl alcohol was recommended by Law-

<sup>224</sup> German P. 363,044, 1920, to A.-G. f. Anilin-fabr.; *J.S.C.I.*, 1923, 42, 366A.

<sup>225</sup> G. Flumiani, *Kolloid-Z.*, 1928, 45, 183; *Chem. Abs.*, 1928, 22, 4031.

<sup>226</sup> G. Flumiani, *Z. Elektrochem.*, 1926, 32, 221; *Chem. Abs.*, 1926, 20, 2815.

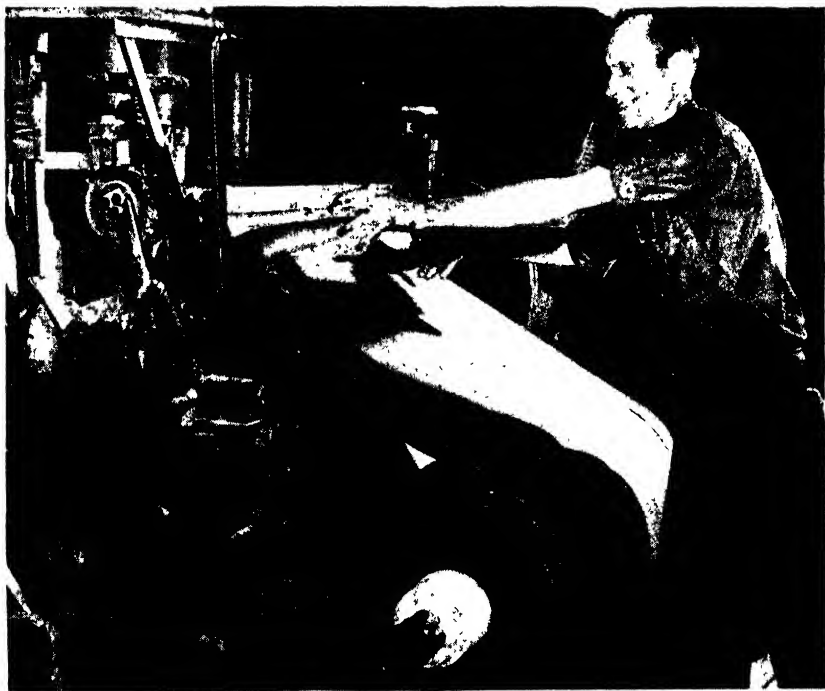
<sup>227</sup> I. Ostromislensky, U. S. P. 1,721,034, July 16, 1929; *Chem. Abs.*, 1929, 23, 4228. British P. 235,537, 1926, to L. A. Van Dyk; *Chem. Abs.*, 1927, 21, 2906.

<sup>228</sup> I. Ostromislensky, U. S. P. 1,791,009, Feb. 3, 1931, to L. A. Van Dyk; *Chem. Abs.*, 1931, 25, 1536. British P. 200,550, 1925; *Chem. Abs.*, 1927, 21, 3369.

<sup>229</sup> W. E. Lawson and J. H. Werntz, British P. 319,591, 1929, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1931, 666. French P. 553,125, 1929; *Chem. Abs.*, 1930, 24, 4806.

<sup>230</sup> W. L. Semon, U. S. P. 1,968,949, Dec. 11, 1934, to B. F. Goodrich Co.; *Chem. Abs.*, 1935, 29, 980.

son<sup>221</sup> as a high-boiling solvent for brushing-lacquers containing polyvinyl chloride. The  $\beta$ -polymer is partially soluble in this liquid. Dibenzylin (dibenzyl ether of glycerol) can be used as a plasticizer, the addition of 1 part of this ether to 3 parts of the  $\alpha$ -polymer yielding soft and flexible films.<sup>222</sup> The  $\alpha$ -polymer is also compatible with drying oils and may be blended with them to form a varnish.<sup>223</sup> Dykstra<sup>224</sup> recommended  $\alpha$ -polyvinyl chloride, polyvinyl chloroacetate and other resins containing chlorine as fluxes for soft soldering.



Courtesy Plastics Division, Carbide and Carbon Chemicals Corp.

FIG. 135.—Rubberless Army Raincoats Made by U. S. Rubber Company.

As mentioned above, ozone is a catalyst for the polymerization of vinyl chloride. In using ozone, air containing it is passed through a solvent for 2 hours, after which the vinyl compound is added. For example, Lawson<sup>225</sup> dissolved 17 g. of vinyl chloride in 69 g. of ozonized methanol and heated the solution for 5 hours in a sealed tube at 120°C. He obtained 7 g. of resin, composed entirely of the  $\alpha$ -polymer. In place of heating, the solution can be exposed to sunlight. A small proportion of water in the solvent has no adverse influence on the reaction. Hydro-

<sup>221</sup> W. E. Lawson, U. S. P. 1,780,652, Nov. 4, 1930, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 222. *British P.* 312,049, 1929; *Brit. Chem. Abs. B.*, 1930, 872.

<sup>222</sup> H. B. Dykstra and W. E. Lawson, U. S. P. 1,806,152, May 19, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 3784. *British P.* 349,562, 1929; *Brit. Chem. Abs. B.*, 1931, 729. *French P.* 685,821, 1929; *Chem. Abs.*, 1930, 24, 5951.

<sup>223</sup> W. E. Lawson, *British P.* 312,344, 1929, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B.*, 1931, 72. *Canadian P.* 315,870, 1931, to Canadian Industries, Ltd.; *Chem. Abs.*, 1932, 26, 1460.

<sup>224</sup> H. B. Dykstra, U. S. P. 1,800,445, Apr. 14, 1931, to Grasselli Chemical Co.; *Brit. Chem. Abs. B.*, 1932, 112.

<sup>225</sup> W. E. Lawson, U. S. P. 1,890,060, Dec. 6, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1659. *British P.* 319,587, 1928; *Chem. Abs.*, 1930, 24, 2470. *French P.* 682,127, 1929; *Chem. Abs.*, 1930, 24, 4308.

chloric acid (about 0.5 per cent) also has a catalytic effect. Using such a small amount of acid, the color of the polymer is not darkened appreciably.<sup>280</sup> Larger proportions of acids may be employed provided ethylene oxide is the solvent.<sup>287</sup> Young and Douglas<sup>288</sup> employed lead tetraethyl as a catalyst. A mixture of 70 parts of vinyl chloride, 30 parts of acetone and 1.4 parts of lead tetraethyl was heated in an autoclave for 20 hours at 80°C. A white, viscous resin solution was obtained.

The four forms of polyvinyl chloride described by Ostromislensky are insoluble in aromatic hydrocarbons. Lawson and Wernitz<sup>289</sup> have obtained a new form, lower in the polymeric series than the  $\alpha$ -form, by dissolving vinyl chloride in a benzenoid hydrocarbon, adding a catalyst and heating the solution. A mixture of 1500 parts by weight of vinyl chloride, 1000 parts of toluene and 45 parts of benzoyl peroxide was passed through a long lead-lined tube at 115-120°C. under a pressure of 500 pounds per square inch furnished by nitrogen gas. Seventeen hundred and seventy parts by weight of a light brown solution were obtained, having an acid number of 6, a viscosity of about 0.5 poise at 20°C. and containing 42.6 per cent solids. This was equivalent to a yield of 50.3 per cent of toluene-soluble polyvinyl chloride. The new polymer gave solutions of much lower viscosity than the other forms. While a 30 per cent solution of the  $\alpha$ -polymer is a gel at room temperature, the hydrocarbon-soluble polymer in ethyl acetate showed a low viscosity. It also differed from the  $\alpha$ -polymer in being incompatible with drying oils. A formula for an enamel containing this polymer consists of 16 parts of resin, 2 parts of dibutyl phthalate, 36 parts of solvent naphtha, 27 parts of toluene and 19 parts of titanium dioxide.<sup>290</sup>

A method for obtaining more uniform products of a high degree of polymerization has been suggested by Klatte and Müller.<sup>281</sup> They stopped the reaction and distilled off the monomeric form when there was yet about 50 per cent of it present. This procedure was found to permit a more uniform distribution of the catalyst and more exact separation of the remaining monomeric vinyl halide. For example, 1000 parts of vinyl chloride were passed in the gaseous state through a quartz tube illuminated by a mercury-vapor lamp. After recondensation of gas to the liquid state, 10 parts of barium peroxide and 10 parts of acetic anhydride were added. The mixture was heated in an autoclave for 10 hrs. at 35-45°C. The monomeric form was distilled off leaving about 350 parts of pulverulent, white polymer. Under the same conditions without the irradiation only about 250 parts of polyvinyl chloride were produced.

Vinyl halides, either alone or mixed with other polymerizable substances, may be polymerized while emulsified in water.<sup>282</sup> By coagulating the dispersion of rubber and polyvinyl halide formed by mixing a vinyl halide with latex and then polymerizing, plastic masses have been formed.<sup>283</sup> By heating vinyl halides under pressure, Voss and Dickhäuser prepared substances resembling celluloid.<sup>284</sup>

Prolonged heating of vinyl chloride in a closed vessel with a catalyst results in a polymer of the insoluble type. The reaction is more rapid if the vinyl chloride

<sup>280</sup> French P. 712,263, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 2073.

<sup>287</sup> J. H. Wernitz, U. S. P. 1,983,529, Jan. 22, 1935, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 1141.

<sup>288</sup> C. O. Young and S. D. Douglas, U. S. P. 1,775,882, Sept. 16, 1930, to Carbide & Carbon Chem. Corp.; *Chem. Abs.*, 1930, 24, 5308.

<sup>289</sup> W. E. Lawson and J. H. Wernitz, U. S. P. 1,874,107, Aug. 30, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 5965. French P. 709,562, 1931; *Chem. Abs.*, 1932, 26, 1299.

<sup>290</sup> British P. 579,292, 1931, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1933, 997. French P. 717,886, 1931; *Chem. Abs.*, 1932, 26, 2379.

<sup>281</sup> F. Klatte and H. Müller, U. S. P. 1,920,408, Aug. 1, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4816. British P. 358,004, 1933; *Chem. Abs.*, 1933, 27, 4251.

<sup>282</sup> French P. 748,969, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4816.

<sup>283</sup> French P. 763,460, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5716. British P. 412,501, 1933; *Brit. Chem. Abs. B*, 1934, 773.

<sup>284</sup> A. Voss and E. Dickhäuser, German P. 579,048, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4948.



is first exposed to the rays from a mercury arc.<sup>285</sup> Resins of which more than 75 per cent are insoluble in toluene have been prepared by heating vinyl chloride in a liquid the solvent power of which toward the resinous product is not appreciably more than that of toluene, e.g., an aliphatic hydrocarbon or alcohol. The temperature is kept below 60°C.<sup>286</sup>

Staudinger, Brunner and Feisst<sup>287</sup> investigated the polymerization of vinyl bromide and chloride exposed to ultraviolet light. The latter compound, for example, yielded polymers which were not soluble in the monomer, therefore no viscous solution or syrupy liquid was formed as the first step. Instead, there was separation of a solid phase, a mixture of low and high polymeric halides. Usually the average degree of polymerization was about 50, i.e., the union of about 50 molecules of vinyl chloride. The structure of polyvinyl chloride is represented as a long chlorinated hydrocarbon chain



in which the end groups are combined with solvent molecules, catalyst groups, or possibly are saturated by formation of rings.<sup>288</sup> The lower members of the polymer series are the more soluble and can be partially separated by fractional solubility in benzene or carbon disulphide. Molecular-weight determination is difficult on account of the low solubility in the cold, and, if the solution is heated to aid solubility, the polymer breaks down easily. These polymers are also sensitive to light and become discolored after a time. Soluble polyvinyl halides are of the hemi-colloid type and the highest polymer that could be obtained had a degree of polymerization of 100. Above this value the polymers are insoluble and correspond to the  $\gamma$ -polymer of Ostromislensky. The polymers produced by irradiating solutions of vinyl halides are more soluble than those prepared from the pure halides. It seems to be a general rule that dilution lowers the degree of polymerization of the product.

#### POLYMERIZATION OF OTHER HALOGEN-SUBSTITUTED ETHYLENES

Vinyl bromide is similar to vinyl chloride in the readiness with which it polymerizes, the change occurring when the liquid is exposed to sunlight.<sup>289</sup> The polymer is a solid, amorphous body, insoluble in water, alcohol and ether. The specific gravity of the material is 2.075. Boiling alcoholic potash extracts no bromine unless the treatment is continued for a very long time. The presence of light volatile hydrocarbons greatly retards the polymerization,<sup>290</sup> and, according to Kutscherow,<sup>291</sup> a trace of iodine hinders the reaction in diffused light.

Besides vinyl chloride and vinyl bromide, certain of the other halogenated ethylenes show a tendency towards polymerization. This applies, however, only to the dihalogen compounds of unsymmetrical structure,<sup>292</sup> such as  $\text{CH}_2=\text{CCl}_2$ ,  $\text{CH}_2=\text{CBr}$ , and  $\text{CH}_2=\text{CClBr}$ . Symmetrically substituted compounds like  $\text{CHCl}=\text{CHCl}$  and  $\text{CHBr}=\text{CHBr}$  are relatively stable, as is also trichloroethylene,  $\text{CHCl}=\text{CHCl}=\text{CHCl}$ .

<sup>285</sup> French P. 719,032, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 3344.

<sup>286</sup> E. W. Reid, British P. 406,338, 1914, to Carbide & Carbon Chem. Corp.; *Chem. Abs.*, 1924, 28, 4924. French P. 741,657, 1932; *Chem. Abs.*, 1933, 27, 2831.

<sup>287</sup> H. Staudinger, M. Brunner and W. Feisst, *Helv. Chim. Acta*, 1930, 13, 805, *Chem. Abs.*, 1931, 25, 487.

<sup>288</sup> I. Ostromislensky, *J. Russ. Phys.-Chem. Soc.*, 1912, 44, 204; *J.C.S.*, 1912, 102 (1), 280, suggested a similar structure for the polymer of vinyl bromide.

<sup>289</sup> E. Baumann, *Ann.*, 1872, 163, 312; *Chem. Zentr.*, 1873, 28. M. Lwow, *Ber.*, 1873, 11, 1258.

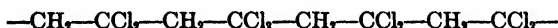
<sup>290</sup> I. Ostromislensky, *J. Russ. Phys.-Chem. Soc.*, 1912, 44, 204; *J.C.S.*, 1912, 102 (1), 280.

<sup>291</sup> M. Kutscherow, *Ber.*, 1931, 14, 1333.

<sup>292</sup> Cf. B. T. Brooks, "The Non-Benzenoid Hydrocarbons," Chemical Catalog Co., New York, 1923, 211.

$\text{CCl}_2$ , which is not spontaneously polymerized or oxidized when kept in contact with oxygen. The group,  $\text{CH}_2=\text{C}=\text{}$ , is apparently necessary for this type of polymerization. Compounds of fluorine and iodine are more stable than those of the other halogens. For example, vinyl iodide<sup>344</sup> oxidizes easily but does not readily polymerize, whereas difluoroethylene,  $\text{CH}_2=\text{CF}_2$ , undergoes neither of these reactions. When one of the fluorine atoms is replaced by bromine to form fluorobromoethylene,  $\text{CH}_2=\text{CFBr}$ , the resulting product is easily oxidized and polymerizes to a solid body.<sup>345</sup> Chlorobromoethylene,  $\text{CH}_2=\text{CClBr}$ , quickly changes to a solid, amorphous polymer. Biltz<sup>346</sup> allowed its polymerization to progress for 8 days, obtaining a polymer,  $(\text{CH}_2=\text{CClBr})_x$ , insoluble in most of the common solvents. It is slightly soluble in hot nitrobenzene and in molten naphthalene. Dibromoethylene,  $\text{CH}_2=\text{CBr}_2$ , is a liquid which easily changes to a polymeric solid of density 3.053, insoluble in water, alcohol and ether.<sup>347</sup> Chloronitroethylene,  $\text{CH}_2=\text{CClNO}_2$ , in the presence of sodium bicarbonate, is also transformed into a solid.<sup>347</sup>

Staudinger and Feisst<sup>348</sup> studied the polymerization of asym-dichloroethylene.<sup>349</sup> This liquid polymerizes very quickly in the light but also to the extent of 90 per cent when kept for 6 days in the dark. The polymer is very similar to polyvinyl chloride in appearance and in solubility, and its structure is represented as a long chain:



The number of groups of the monomer,  $-\text{CH}_2-\text{CCl}_2-$ , in the chain is between 50 and 100. The polymeric material is completely saturated. When heated above  $120^\circ\text{C}$ . it chars and some hydrogen chloride is eliminated. When reduced with red phosphorus and 70 per cent hydriodic acid at  $170^\circ\text{C}$ ., it formed a mixture of hydrocarbons which could be separated into two fractions, one having a molecular weight of 1400-1500 and the other having one of about 2400. This is considered significant evidence that the polymer consists of a long chain-structure. When the polymer is heated with aniline for 14 days, almost complete elimination

of halogen is accomplished and a benzene-soluble product,  $(-\text{CH}_2-\overset{\textstyle |}{\text{C}}=\text{NC}_6\text{H}_5)_x$ , results.

#### USE OF VINYL HALIDE RESINS

Vinyl halide resins, plasticized with various agents, such as tung or other natural drying oils<sup>350</sup> (particularly when blown), waxes and dialkyl phthalates,<sup>351</sup> or condensation products of polybasic acids, polyhydric alcohols and monobasic acids<sup>352</sup> (containing more than 6 carbon atoms), have been employed as coating agents. One coating composition, for example consisted of 16 parts of polyvinyl chloride (soluble in toluene), 19 parts of titanium oxide, 2 parts of dibutyl phthalate, 36 parts of solvent naphtha and 27 parts of toluene.<sup>353</sup> Another preparation con-

<sup>344</sup> J. Spence, *J.A.C.S.*, 1923, 55, 1390.

<sup>345</sup> F. Swarts, *Bull. Sci. Acad. roy. Belg.*, 1909, 728. *Chem. Zentr.*, 1909, 2, 1414.

<sup>346</sup> H. Biltz, *Ber.*, 1902, 35, 3527.

<sup>347</sup> Sawitch, *Jahresber.*, 1860, 431.

<sup>348</sup> R. Wilkendorf and M. Trenel, *Ber.*, 1924, 57, 306; *Chem. Abs.*, 1924, 18, 2129.

<sup>349</sup> H. Staudinger and W. Feisst, *Helv. Chim. Acta*, 1930, 13, 832; *Brit. Chem. Abs. A*, 1930, 1402.

<sup>350</sup> Asym-dichloroethylene is obtained as a by-product in the preparation of trichloroethylene.

<sup>351</sup> W. E. Lawson, U. S. P. 1,938,662, Dec. 12, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1557.

<sup>352</sup> F. H. Reichel, British P. 359,914, 1933; *Chem. Abs.*, 1933, 27, 4699.

<sup>353</sup> French P. 772,852, 1924, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1925, 29, 1667.

<sup>354</sup> French P. 717,826, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 2879. British P. 379,292, 1933; *Chem. Abs.*, 1933, 27, 4107.

tains an ester polymerized in ethylbenzene, in the presence of nitrocellulose, rosin and tung oil.<sup>263</sup>

Stelkens<sup>264</sup> described a viscous solution containing rubber, cellulose derivatives and polyvinyl chloride for sticking patches to worn places in clothing. An application of polyvinyl chloride as photographic film has been suggested by Stinchfield,<sup>265</sup> who used a layer of the polymerized chloride, coated on both sides with cellulose acetate to inhibit static charges. The sensitive emulsion is applied over the cellulose acetate. Resins which have sufficient solubility and mechanical



*Courtesy Plastics Division, Carbide and Carbon Chemicals Corp.*

FIG. 136.—Melting a Compounded Vinylite Resin.

strength for making films and lacquers have been obtained by chlorinating a hot solution or suspension of polyvinyl chloride in swelling agents such as carbon tetrachloride or tetrachloroethane.<sup>266</sup> The mechanical properties of sheets or films of polyvinyl chloride are improved by extracting the unevaporated solvent with benzene or methyl alcohol, which do not dissolve the resin.<sup>267</sup>

A method of evaluating samples of polyvinyl chloride for use in the above

<sup>263</sup> W. E. Lawson and L. T. Sandborn, U. S. P. 1,975,959, Oct. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 7562.

<sup>264</sup> W. Stelkens, German P. 470,149, 1927; *Chem. Abs.*, 1929, 23, 1482.

<sup>265</sup> R. L. Stinchfield, U. S. P. 1,627,935, May 10, 1927, to Eastman Kodak Co.; *Brit. Chem. Abs. B*, 1927, 718. The salts of polymeric carboxylic acids, e.g., polyglycuronic acid and polycinnamic acid, have been used for this purpose (British P. 411,689, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1934, 733).

<sup>266</sup> C. Schönburg, U. S. P. 1,982,765, Dec. 4, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 836. British P. 401,200, 1933; *Brit. Chem. Abs. B*, 1934, 29. French P. 755,048, 1933; *Chem. Abs.*, 1934, 28, 1485. German P. 896,911, 1934; *Chem. Abs.*, 1934, 28, 5190.

<sup>267</sup> British P. 394,244, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 371. French P. 746,905, 1933; *Chem. Abs.*, 1933, 27, 4642.

applications is the determination of the solubility in a 3 to 1 mixture of chlorobenzene and epichlorohydrin. It should take at least 15 cc. of the hot mixture to dissolve 1 g. and hold it in solution for 5 minutes after cooling to 20°C.<sup>598</sup>

Vinyl chloride polymers may be compounded with flexible alkyd resins<sup>599</sup> and fillers by heating at approximately 95°C. for ½ hour. After shaping, the product is cured for about 22 hours at 80-100°C.<sup>600</sup> Semon<sup>601</sup> prepared a resilient, rubber-like composition by dissolving 1 part of highly polymerized vinyl chloride at an elevated temperature in 0.5-4.0 parts of solvent which consisted of 2 parts of o-nitrodiphenyl ether and 1 part each of dinitrobenzene and dinitrotoluene. On cooling, the solution gelled and then was a corrosion-resistant electrical insulator. Thompson<sup>602</sup> has suggested a method of attaching such rubber-like materials to metals. He made a glue by mixing some of the polyvinyl halide with a fusible resin and then dissolving the mixture in a solvent. This glue was applied to the metal and the solvent allowed to evaporate. Then the rubber-like material was pressed on and the joint heated. One class of insoluble polyvinyl halide plastics (Koroseal) includes compositions of translucent appearance possessing colors ranging from pale amber to dark brown. The properties vary from those of hard rubber to those of gelled rubber cement. These plastics have exhibited good resistance to aging and light-cracking.<sup>603</sup>

Melamid<sup>604</sup> obtained a substitute for linseed oil by the reaction at 100°C. of allyl or vinyl bromide and solutions of hydroxybenzyl alcohols (from m- and p-cresols and formaldehyde) in 20 per cent aqueous caustic soda. The product was diluted with water and the solution extracted with ether or acetone. After distilling off the solvent, a viscous light brown liquid was obtained which solidified in the air. Any initial condensation product of a phenol with formaldehyde may be further treated in alkaline solution in this manner, and the allyl or vinyl ethers of dihydroxydiarylmethane thus formed are clear viscous transparent liquids, solidifying on exposure to the air.<sup>605</sup> Plauson<sup>606</sup> also made a composite vinyl chloride-phenol-formaldehyde resin by incorporating the chloride with the phenol resin at the time of its formation. A mixture of 94 parts of phenol, 65 parts of hexamethylenetetramine and 65 parts of polymerized vinyl chloride was stirred and heated to about 80°C. An exothermic reaction occurred and finally a clear, homogeneous liquid was obtained which gradually changed into a solid, tough mass.<sup>607</sup> Vinyl chloride has been condensed with phenols in the presence of aluminum or ferric chloride and the products polymerized by ultraviolet light.<sup>608</sup>

Voss and Dickhäuser<sup>609</sup> made a heteropolymer by heating a mixture of 80 parts of vinyl chloride, 100 parts of maleic anhydride, 0.5 part of barium peroxide

<sup>598</sup> French P. 744,229, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4100.

<sup>599</sup> See Chapter 45.

<sup>600</sup> J. G. E. Wright, British P. 387,928, 1932, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs.*, B, 1933, 317. See also German P. 601,323, 1934, to Allgemeine Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 7564.

<sup>601</sup> W. L. Semon, U. S. P. 1,929,453, Oct. 10, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1934, 28, 371. Canadian P. 289,377, 1934; *Chem. Abs.*, 1934, 28, 2947. British P. 398,091, 1933; *Brit. Chem. Abs.*, B, 1933, 330.

<sup>602</sup> O. A. Thompson, U. S. P. 1,931,809, Oct. 17, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1934, 28, 374. British P. 383,776, 1933; *Chem. Abs.*, 1933, 27, 5909.

<sup>603</sup> S. L. Brous and W. L. Semon, *Ind. Eng. Chem.*, 1935, 27, 667; *British Plastics*, 1935, 7, 55.

<sup>604</sup> M. Melamid, German P. 332,003, 1920; *J.S.C.I.*, 1922, 41, 738A.

<sup>605</sup> German P. 436,445, 1921, addn. to 352,003, 1920, to A. Riebeck'sche Montanwerke A.-G.; *Brit. Chem. Abs.*, B, 1927, 292.

<sup>606</sup> H. Plauson, U. S. P. 1,451,943, Apr. 17, 1923; *Chem. Abs.*, 1923, 17, 2058. Canadian P. 226,633, 1923; *Chem. Abs.*, 1923, 17, 1187. British P. 156,151, 1920, to H. O. Traun's Forschungslaboratorium G.m.b.H.; *J.S.C.I.*, 1922, 41, 351A. German P. 264,045, 1918, to Plauson's Forschungsinstitut G.m.b.H.

<sup>607</sup> For lacquers consisting of solutions of polymerized vinyl halides and phenol-aldehyde condensation products, see British P. 312,549, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2317. French P. 680,877, 1929; *Chem. Abs.*, 1930, 24, 4123.

<sup>608</sup> British P. 409,133, 1939, to British Celanese, Ltd.; *Brit. Chem. Abs.*, B, 1934, 594.

<sup>609</sup> A. Voss and E. Dickhäuser, German P. 340,101, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1813. British P. 376,479, 1931; *Brit. Chem. Abs.*, B, 1932, 943. French P. 719,145, 1931.

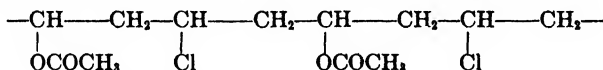
and 1.2 parts of acetic anhydride in an autoclave for 16 hours at 80°C. The product was a white powder, soluble in water and containing 14 per cent chlorine. Jordan, Hopff and Kühn have prepared heteropolymers of vinyl halides, or vinyl cyanide and stand oils.<sup>300</sup>

When benzene is treated with vinyl chloride in the presence of aluminum chloride at a low temperature, the main products are asym-diphenylethane and an anthracene-type resin. A trace of iodine causes a decrease in the amount of resin.<sup>301</sup> According to Dreyfus,<sup>301</sup> polymerized 2-chloropropene heated with a solution of disodium tartrate furnishes an impregnating and sizing agent. In this instance the chlorine is replaced by a tartrate radical.

Adhesives may be obtained by subjecting polyvinyl chloride to a complementary chlorination,<sup>302</sup> or by depolymerization of the chlorinated material (effected by heating) and incorporating wetting agents.<sup>303</sup>

### CO-POLYMERIZATION OF VINYL ESTERS

The most important vinyl ester co-polymer is that obtained by polymerization of a mixture of vinyl chloride and vinyl acetate.<sup>304</sup> The resulting resin differs from the polymer of either co-reactant and in many respects is superior to either. It also differs from a mixture of the polymers prepared separately and blended. When equivalent amounts of each component are mixed and polymerized, the structure of the co-polymer may be pictured as a long chain, the alternate links of which are vinyl chloride and vinyl acetate units:



In general, the actual distribution of the components in the chain is dependent entirely on chance collisions and on the relative proportions of the reactants.

### POLYMERIZATION

A mixture of vinyl chloride and acetate can be polymerized in any way applicable to the two reactants alone, that is, by the action of heat or light in the presence of a catalyst. Lawson<sup>305</sup> has described a continuous process for producing the co-polymers dissolved in a liquid by passing a heated solution of the two vinyl compounds through a long tube under pressure.

A mixture of 60 parts by weight of ethyl acetate, 30 parts of vinyl chloride, 10 parts of vinyl acetate and 2.7 parts of benzoyl peroxide was forced through a lead-lined, steel reaction-tube having a volume of 800 cc. at a pressure of 200 pounds per square inch. The rate of flow was 800 cc. per hour and the temperature 120°C. The interpolymerized product obtained in this manner gave a slightly yellow solution which yielded a white polymer when precipitated with alcohol. The yield of polymer

<sup>300</sup> O. Jordan, H. Hopff and E. Kühn, German P. 580,324, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4943. French P. 749,158, 1933; *Chem. Abs.*, 1934, 28, 350.

<sup>301</sup> J. M. Davidson and A. Lowy, *J.A.C.S.*, 1929, 51, 2978.

<sup>302</sup> H. Dreyfus, British P. 385,978, 1932; *Chem. Abs.*, 1933, 27, 4247.

<sup>303</sup> French P. 774,401, Dec. 6, 1934, Dynamit A.-G. vorm A. Nobel & Co.; *Chem. Abs.*, 1935, 29, 2262.

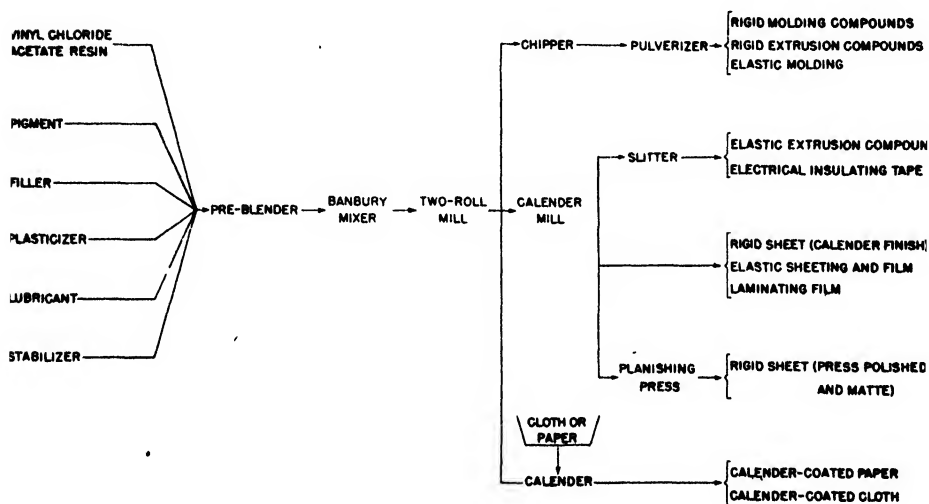
<sup>304</sup> French P. 774,983, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2262. Cf. French P. 755,048, 1933; *Chem. Abs.*, 1934, 28, 1485.

<sup>305</sup> One form of the resin known as Vinylite, made by Carbide & Carbon Chemicals Corp., is said to be a co-polymer of vinyl chloride and vinyl acetate. The various grades differ in the proportions of the two vinyl compounds used. For the use of Vinylite in the preparation of artificial eyes, see J. L. Travers, U. S. P. 1,993,121, Mar. 5, 1935, to M. H. Russell; and in the manufacture of laminated products, J. D. Cochran, Jr., U. S. P. 1,997,359, Apr. 9, 1935, to the Formica Insulation Co.

<sup>306</sup> W. E. Lawson, U. S. P. 1,867,014, July 12, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 26, 4611. British P. 319,588, 1929; *Brit. Chem. Abs. B*, 1931, 666. French P. 682,123, 1929; *Chem. Abs.*, 1930, 24, 4806.

was 66 per cent, the concentration of vinyl chloride in the material being 72 per cent. In another case a solution of 1000 g. of vinyl chloride, 250 g. of vinyl acetate and 57 g. of benzoyl peroxide in 650 g. of ethyl acetate was forced through the tube. The product was very viscous. The yield of polymer was about 70 per cent and the concentration of vinyl chloride in the resin was 80 per cent.

The polymers from vinyl acetate adhere well to various surfaces, but coatings made from them are too soft and too soluble in common solvents. They are easily scratched and also are damaged by contact with preparations containing alcohols. Polyvinyl halides, on the other hand, give more resistant films, but



Courtesy Plastics Division, Carbide and Carbon Chemicals Corp.

FIG. 137.—Steps in the Manufacture of Vinylite Plastics.

ones which have poor adhesion. Reid<sup>276</sup> reports that the co-polymer of vinyl acetate and chloride is an internally plasticized resin possessing good adherence and which is also tough and strong.

Aqueous emulsions of the mixed polymers have been treated with ammonia or alkali hydroxides.<sup>277</sup> The latter have also been used to partially or completely saponify the heteropolymer.<sup>278</sup> Molding powders with almost impalpable grains of uniform size have been prepared by precipitating the co-polymer from an acetone solution with ammonia or amines.<sup>279</sup> The procedure that has been sug-

<sup>276</sup> E. W. Reid, U. S. P. 1,935,577, Nov. 14, 1933, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1934, 28, 663. See also Frasier Groff, British P. 388,309, 1933, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1933, 27, 4700. French P. 740,962, 1932; *Chem. Abs.*, 1933, 27, 2771.

<sup>277</sup> British P. 410,132, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1934, 638.

<sup>278</sup> A. Voss and W. Starck, German P. 555,633, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2457.

<sup>279</sup> C. N. Smith, U. S. P. 1,922,638, Feb. 26, 1935, to National Carbon Co.; *Chem. Abs.*, 1935, 29, 2624.

gested is as follows: 25 grams of dry resin are dissolved in 1 liter of acetone, and 140 cc. of this is run into an agitated mixture of 1280 cc. of water and 320 cc. of ammonium hydroxide, the solution being maintained at 30-35°C. The addition of 5 cc. of concentrated hydrochloric acid flocculates the suspension. The small aggregates obtained after washing and drying are easily broken up.

A low-viscosity vinyl polymer has been prepared by adding rosin to the mixture of vinyl acetate and vinyl chloride before polymerizing.<sup>300</sup> Young and Douglas<sup>301</sup> increased the melting point of the resin resulting from the polymerization of a mixture containing about 80 per cent of vinyl chloride and 20 per cent of vinyl acetate by heating the resin in a liquid medium in the presence of benzoyl peroxide at 65-75°C. They also obtained a substantially uniform vinyl resin of relatively low fusion point by extracting the polymerized mass with toluene in which the desired fraction dissolved.<sup>302</sup>

#### USES OF THE VINYL ACETATE-CHLORIDE CO-POLYMERS

The co-polymers of vinyl chloride and vinyl acetate may be roughly divided into two groups: one containing a major proportion of vinyl acetate, making them applicable for coatings where adequate solubility is required, and the other containing a major proportion of vinyl chloride, more suitable for molding purposes.<sup>303</sup>

Co-polymers may be fractionated by extraction with solvents.<sup>304</sup> Thus an insoluble gel precipitates from a mixture of toluene (90 parts) and resin (10 parts). The soluble fraction has an average molecular weight of 1500 and melts at 60-80°C. The insoluble portion has an average molecular weight of 2500 and does not melt below 125°C. The latter fraction gives films which have greater strength and are tougher and more resistant to heat than the original polymer. The soluble portion may be used for coatings and the insoluble fraction for moldings such as dentures.<sup>305</sup>

#### COATINGS

If 30 parts of vinyl chloride and 70 parts of vinyl acetate are polymerized together, a resin is formed which is soluble in such solvents as toluene, benzene and butyl acetate, and which is less inflammable than polyvinyl acetate alone. The resin is compatible with nitrocellulose and can be used in lacquers.<sup>306</sup> A wax added to such a lacquer increases its water-resistance.<sup>307</sup> The paper liners for closures to food containers have been coated with a plasticized vinyl acetate-chloride resin.<sup>308</sup>

Lacquers having a vinyl chloride-vinyl acetate-resin base show promise in several directions. They are stable to light and resistant to ordinary salt and alkaline

<sup>300</sup> H. J. Barrett, U. S. P. 1,942,531, Jan. 9, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 1717.

<sup>301</sup> M. K. Young and S. D. Douglas, Canadian P. 328,051, 1932, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1933, 27, 1219.

<sup>302</sup> M. K. Young (executrix for C. O. Young) and S. D. Douglas, Canadian P. 333,391, 1933, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1933, 27, 4701.

<sup>303</sup> An article illustrating the uses of vinyl resins has been contributed by J. G. Davidson and H. B. McClure (*Ind. Eng. Chem.*, 1933, 25, 645).

<sup>304</sup> C. O. Young and S. D. Douglas, U. S. P. 1,990,685, Feb. 12, 1935, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1935, 29, 2261. Canadian P. 333,391, 1933; *Chem. Abs.*, 1933, 27, 4701.

<sup>305</sup> F. Groff, U. S. P. 1,990,903, Feb. 12, 1935, to Carbide & Carbon Chemicals Corp.

<sup>306</sup> J. G. Davidson, U. S. P. 1,838,368, Dec. 29, 1931, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1932, 26, 1460. British P. 235,049, 1927; *Brit. Chem. Abs.*, B, 1929, 219. French P. 640,364, 1927; *Chem. Abs.*, 1929, 23, 999. Canadian P. 278,931, 1928; *Chem. Abs.*, 1928, 22, 2850. German P. 590,858, 1934; *Chem. Abs.*, 1934, 28, 3255.

<sup>307</sup> F. H. Reichel, British P. 389,914, 1931; *Brit. Chem. Abs.*, B, 1933, 436. Canadian P. 332,536, 1933, to Sylvania Industrial Corp.; *Chem. Abs.*, 1933, 27, 4109. French P. 728,189, 1931; *Chem. Abs.*, 1932, 26, 8777.

<sup>308</sup> D. M. Gray, U. S. P. 1,903,319, April 4, 1933, to Hazel-Atlas Glass Co.; *Chem. Abs.*, 1933, 27, 3333.

solutions and to acid solutions of concentration up to about 20 per cent.<sup>299</sup> As a paint for plastered walls, a vinyl-resin lacquer has been found to give good coverage per gallon. No "sealer" is necessary. An increased coverage which is sometimes found may be due to the fact that the lacquer does not penetrate but tends to stay at the surface. The dense film thus formed is reported to be easier to keep clean than the more porous film of ordinary paint.

### MOLDINGS

One disadvantage of polyvinyl chloride as a molding resin is its tendency to decompose at the temperature required in the molding operation. This decomposition is especially troublesome in the presence of iron and iron compounds, and it is necessary to avoid fillers containing iron, such as the usual calcined filler containing hematite. The iron compound is attacked, forming ferric chloride which causes the mass to become porous and brittle during the mixing process. The addition of 10 per cent of vinyl acetate to the chloride before polymerization produces a resin which is much more stable than polyvinyl chloride alone. Although polyvinyl acetate is not as resistant to moisture as might be desired, the small amount required in conjunction with polyvinyl chloride does not seriously affect the co-polymer in this respect. Co-polymers containing a high proportion of the chloride find application in such fields as dentures,<sup>300</sup> and sound records.<sup>301</sup>

As a material for sound records vinyl resin has partially replaced two plastics: (1) shellac formerly used in making standard records, vinyl resin showing a better quality of tone, and (2) celluloid as used for home recording, where the advantage of vinyl resin from the standpoint of fire hazard is obvious. The vinyl compound gives a quieter record and one which is much lighter. The old 16-inch record weighed 20 ounces, while the 12-inch vinyl record having the same playing time weighs only 4 ounces. Shellac records require very careful packing in wooden boxes but the vinyl records, owing to their flexibility, can be packed in paper boxes. The addition of a filler to the vinyl resin is desirable, as it gives a cheaper composition with improved resistance to wear by the needle. In order to make a satisfactory filled compound it is necessary to add plasticizers. Solid Aroclors and Halowaxes are commonly used but others, such as dibutyl phthalate and triphenyl phosphate, produce similar results although they are more expensive.

A variety of articles have been fabricated from these resins. For example, Groff has prepared sound records, linoleum and a transparent, flexible wrapping material. He used 80 parts of vinyl chloride and 20 parts of vinyl acetate and graded the product by the solubility in toluene.<sup>302</sup> The resin may be mixed with a filler, e.g., silica or mica, or a plasticizer, e.g., dibutyl phthalate.<sup>303</sup> Stabilizers, which may be incorporated also, include alkaline earth metal soaps, resinates, oxides or carbonates, aromatic amines which are insoluble in water<sup>304</sup> and olefin oxides such

<sup>299</sup> G. F. Steigerwalt (*Agr. Eng.*, 1933, 14, 154; *Chem. Abs.*, 1934, 28, 873) has reported that Stonite (a Vinylite coating material) is a satisfactory coating for silo walls.

<sup>300</sup> Two dentures on the market having a basis of Vinylite are known as Vidon and Resovin. See also N. B. Nabbett, *Dental Cosmos*, 1933, 75, 1035; *Chem. Abs.*, 1934, 28, 1536. For the preparation of dentures, see F. Groff, U. S. P. 1,990,903, Feb. 12, 1935, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1935, 29, 2361. French P. 745,661, 1934; *Chem. Abs.*, 1934, 28, 6593. F. Schmidt (British P. 412,442, 1934; *Chem. Abs.*, 1934, 28, 7443) reported that co-polymers, which have subsequently been halogenated, may be used also for dentures.

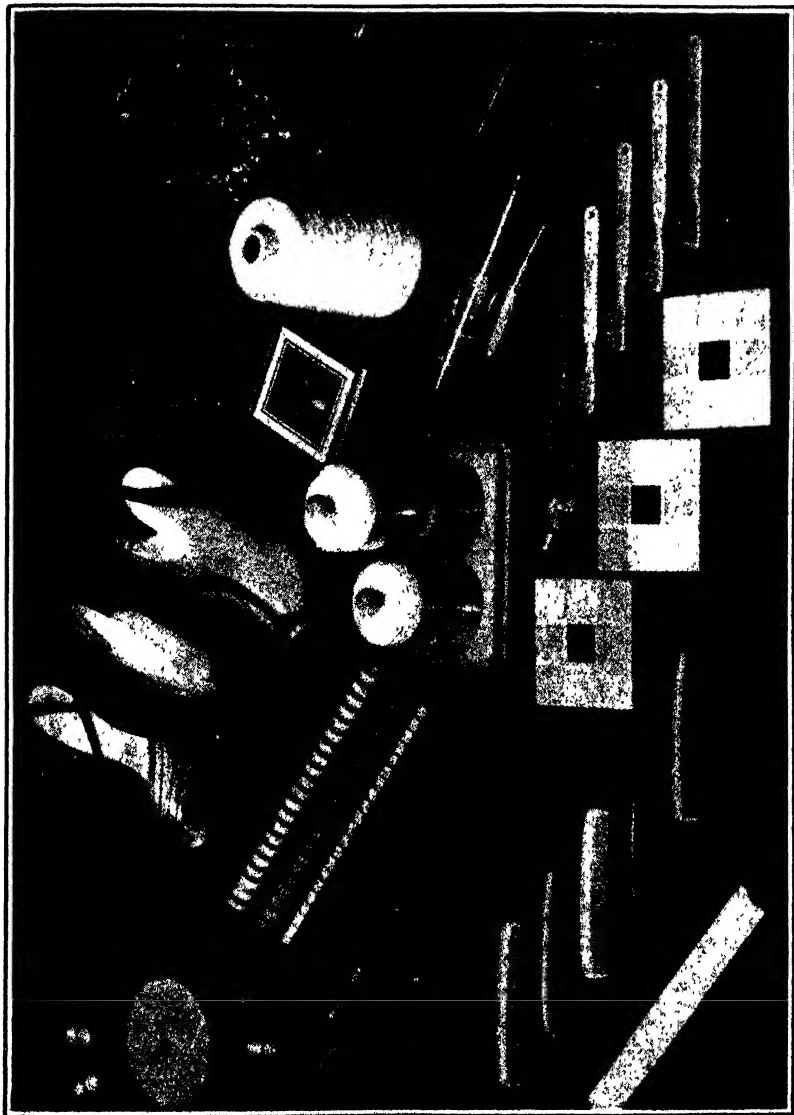
<sup>301</sup> Victrolac, of the Victor Talking Machine Co.

<sup>302</sup> F. Groff, U. S. P. 1,932,839, Oct. 31, 1933, and 1,966,856, July 17, 1934, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1934, 28, 598, 5941. British P. 335,309, 1933; *Chem. Abs.*, 1933, 27, 4700. French P. 740,523, 1933; *Chem. Abs.*, 1933, 27, 2771.

<sup>303</sup> H. E. Hofmann, British P. 408,969, 1934, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1934, 28, 6004.

<sup>304</sup> F. Groff, Canadian P. 346,164, 1934, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1935, 29, 3360.





as epichlorohydrin or phenoxypropene oxide.<sup>305</sup> Davidson and McClure<sup>306</sup> report that one advantage Vinylite resins have as dentures is the fact that they are not thermosetting and so may be repaired and remolded repeatedly. Davidson and McClure also describe the construction of a model three-room apartment using Vinylite for windows, doors, flooring, walls and furnishings.

### COMMON USES OF VINYL RESINS

In the preceding sections, mention has been made of certain uses to which the various vinyl resins have been applied. A few investigators have suggested uses to which several or all types of vinyl resins are adapted. These applications may be classified as coating agents,<sup>307</sup> impregnating agents, adhesives and moldings.<sup>308</sup>

### COATING AND IMPREGNATING AGENTS

Solvents in which the various resins will dissolve have been mentioned previously. It has also been noted that plasticizers may, or may not, be used with vinyl resins, depending upon the requirements of the coating. Among the plasticizers which may be employed are the phthalic esters such as dibutyl, dicyclohexyl, diethyl, cyclohexyl butyl or cyclohexyl amyl phthalates<sup>309</sup> and the benzyl ethers of glycerol such as dibenzylin.<sup>300</sup> Derivatives of aromatic sulphonamides (Abracols),<sup>301</sup> tributyl phosphate (Plastoflex), tricresyl phosphate (Lindol),<sup>302</sup> butyl stearate, camphor, triacetin and ethylacetanilide are also compatible with these resins. Moss<sup>303</sup> suggests phenolic derivatives such as diphenylolpropane, diphenylolcyclohexane and triphenyl phosphate.

Another group of substances which can be mixed with vinyl resins include soluble phenol-formaldehyde resins.<sup>304</sup> Among these should be mentioned the condensation products of aldehydes and such phenol derivatives as salicylic acid and phenol ethers.<sup>305</sup> Coating compositions containing vinyl resins, oil-modified alkyl resins and plasticizers have been proposed.<sup>306</sup>

The use of fatty oils as plasticizers without a blending agent should be avoided. However, Carr has made a stencil-sheet composition using dibutyl phthalate and peanut oil.<sup>307</sup> Ten parts of a 30 per cent solution of polyvinyl acetate in toluene were mixed with 3.5 parts of peanut oil, 1 part of dibutyl phthalate and 2 parts of aluminum stearate. The stencil-sheet was then made by applying this mixture to Yoshino paper.

Polyvinyl resins have been suggested by Seel to coat the sides of photographic

<sup>300</sup> British P. 418,330, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1542.

<sup>301</sup> J. G. Davidson and H. B. McClure, *loc. cit.*

<sup>302</sup> G. Fearnley, A. W. Guthrie and J. R. Macauley (*Am. Paint J.*, 1932, 16 (53A), 12, 23, 26; *Chem. Abs.*, 1933, 27, 433) report that priming coats of vinyl resins are not as good as those of natural resins. Reviews on synthetic coatings in general have been contributed by Carleton Ellis (*Ind. Eng. Chem.*, 1932, 25, 125) and by I. Allen, Jr., V. E. Maharg and J. H. Schmidt (*Ibid.*, 1934, 26, 663).

<sup>303</sup> S. N. Ushakov (*J. Chem. Ind. (Moscow)*, 1933, 5, 13; *Chem. Abs.*, 1934, 28, 3533) and S. Malowan (*Kunststoffe*, 1933, 23, 235; *Chem. Abs.*, 1934, 28, 1205) have discussed the use of vinyl resins as molding materials.

<sup>304</sup> British P. 349,100, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 2072. French P. 635,320, 1929; *Chem. Abs.*, 1930, 24, 5951.

<sup>305</sup> H. B. Dykstra and W. E. Lawson, U. S. P. 1,806,152, May 10, 1931, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1931, 25, 3784. British P. 349,562, 1929; *Brit. Chem. Abs. B*, 1931, 729. French P. 635,321, 1929; *Chem. Abs.*, 1930, 24, 5951.

<sup>306</sup> L. Kollek, German P. 578,767, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2773.

<sup>307</sup> British P. 366,461, 1929, divided out of 366,077, 1929, to Celluloid Corp.; *Chem. Abs.*, 1933, 27, 3096.

<sup>308</sup> W. H. Moos, British P. 372,327, 1930, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1932, 807. H. Dreyfus, French P. 727,249, 1931; *Chem. Abs.*, 1932, 26, 5161.

<sup>309</sup> British P. 318,549, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 1120. French P. 630,577, 1929; *Chem. Abs.*, 1930, 24, 4123.

<sup>310</sup> British P. 339,371, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 261.

<sup>311</sup> British P. 425,181, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1935, 465.

<sup>312</sup> K. W. Carr, U. S. P. 1,530,960, Nov. 10, 1931, to Ditto, Inc.; *Chem. Abs.*, 1932, 26, 816.

paper. The emulsion was applied over the vinyl resin. This coating of vinyl compound made the paper waterproof, and therefore the finished print dried faster.<sup>300</sup> Gutta-percha has been mixed with vinyl resins and polymerized oils to form waterproof coatings for use in making sandpaper.<sup>301</sup>

It has been suggested that vinyl halide resins be employed for the impregnation of fabrics, thus rendering them oil-resistant and applicable for covering the vulcanized rubber on insulated wires.<sup>310</sup> Moss used such fabrics also in electrical insulation.<sup>311</sup> He reports that the products are water-resistant. When applied to fabrics made of cellulose acetate the wear-resistance is increased. Also the products have less tendency to slip or ladder. Fabrics thus treated may be used in making the tops for fancy shoes.<sup>312</sup> A composition made from a vinyl resin, a wax, a gum and a plasticizing agent has been suggested for waterproofing cellulose-acetate sheets.<sup>313</sup>

Not only cloth, but also paper has been impregnated with vinyl resins. Lawson reports that paper which has been dipped into solutions of plasticized vinyl resins is stronger than ordinary paper. It is tough and pliable.<sup>314</sup> Groff<sup>315</sup> has added the impregnating agent to the pulp while it was being processed instead of after the paper was finished. Porous paper strengthened with vinyl resins has been used in the manufacture of vacuum-cleaner bags.<sup>316</sup>

Walsh and Caprio<sup>317</sup> introduced an unpolymerized vinyl compound between the layers of materials which they wished to stick together and then polymerized the compound through the action of heat and catalysts. In this manner, they were able to unite wood, metal, rubber, celluloid and ceramic materials. Fife<sup>318</sup> employed polymerized vinyl resins which will flow under heat and pressure to unite the layers of composite sheet materials. Substances like the polyvinyl resins have been used to fasten photographic films to supports so that they can be handled during development.<sup>319</sup> Sound-record disks have been made by attaching the layer on which the sound track is cut with a metal plate using vinyl resins as the adhesive.<sup>320</sup> Vinyl resins have been suggested as binders for the molded calcium-carbide cakes which are used in the generation of acetylene.<sup>321</sup>

As was mentioned under the uses of polyvinyl acetate, considerable work has been done in the attempt to prepare safety glass from vinyl resins. One of the compounds which has been suggested for this purpose is that resulting from the heteropolymerization of methyl acrylate and vinyl cyanide.<sup>322</sup> Similarly, Shep-

<sup>300</sup> P. C. Seel, U. S. P. 1,933,824, Nov. 7, 1933, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 425.

<sup>301</sup> Z. Hadnagy, A. Bouillard and A. Auby, British P. 394,442, 1932; *Brit. Chem. Abs. B*, 1933, 788.

<sup>310</sup> British P. 398,225, 1932, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1933, 1016.

<sup>311</sup> W. H. Moss, British P. 369,944 and 369,945, 1930, to British Celanese, Ltd.; *Chem. Abs.*, 1933, 27, 3090.

<sup>312</sup> British P. 397,711, 1933, to British Celanese, Ltd.; *Chem. Abs.*, 1934, 28, 1202. C. Dreyfus and W. Whitehead, Canadian P. 343,261, 1934, to C. Dreyfus; *Chem. Abs.*, 1934, 28, 7037.

<sup>313</sup> French P. 755,175, 1933, to Carbide & Carbon Chemicals Corp. and Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 1487. M. Jeanny (*Russ.*, 1933, 8, 1017; *Chem. Abs.*, 1934, 28, 2540) has contributed a review on the use of vinyl resins in the sizing of rayons.

<sup>314</sup> W. E. Lawson, U. S. P. 1,953,083, Apr. 3, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3902.

<sup>315</sup> F. Groff, U. S. P. 1,919,697, July 25, 1933, to Carbide & Carbon Chemicals Corp.; *Brit. Chem. Abs. B*, 1934, 464.

<sup>316</sup> British P. 338,258, 1929, to Hoover Co.; *Chem. Abs.*, 1931, 25, 2255.

<sup>317</sup> J. F. Walsh and A. F. Caprio, British P. 308,659, 1928, to Celluloid Corp.; *Chem. Abs.*, 1930, 24, 476.

<sup>318</sup> H. R. Fife, British P. 389,988, 1933, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1933, 27, 5910.

<sup>319</sup> British P. 387,876, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5015. German P. 506,266, 1931; *Chem. Abs.*, 1933, 27, 1116.

<sup>320</sup> British P. 409,560, 1934, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 6259. For the use of polyvinyl compounds as binders for finely divided metals employed in the manufacture of sound records, see British P. 418,096, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1541.

<sup>321</sup> J. G. Davidson and H. F. Robertson, U. S. P. 1,867,985, July 19, 1932, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1932, 26, 5198.

<sup>322</sup> J. S. B. Fleming and A. Renfrew, British P. 398,189, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 1493. See also L. V. D. Scorch and J. Wilson, British P. 389,115, 1933, to Triplex Safety Glass Co., Ltd.; *Chem. Abs.*, 1933, 27, 5920.

pard<sup>322</sup> has used a solution of polyvinyl acetate or the heteropolymer of vinyl acetate and chloride as an optical cement.

Related to the formation of safety glass is the manufacture of glass substitutes. For example, Greider<sup>323</sup> utilized the ultraviolet-transmitting characteristics of polyvinyl esters in the production of a transparent film to be used as a window glass or for light filters. The film was reinforced by supporting it on wire mesh or woven fabric. Plasticizers were mixed with the vinyl resin when it was to be used in this way.<sup>322</sup> Another glass substitute of the same type consisted of wire netting which was coated with a polymerized vinyl compound and then dipped into a cellulose acetate solution to fill in the holes. The vinyl derivative served to protect the wire from the weather.<sup>322</sup>

It has already been mentioned that cellulose esters and ethers can be incorporated into molding compositions made from polyvinyl acetate. One method of mixing any of the vinyl resins with these materials is to polymerize the vinyl ester while in solution with the cellulose compound.<sup>327</sup> Rubber-polyvinyl acetate lacquers have also been mentioned previously. One use to which a mixture of 1 per cent of polymerized vinyl compound with rubber has been applied is as a binder for molding sand. The mixture was dissolved in a volatile solvent along with a sulphur compound to produce vulcanization.<sup>328</sup> Another process in which such mixtures can be used is the manufacture of electrical insulation.<sup>329</sup> A leather substitute comprises rubber together with a resin resulting from the co-polymerization of vinyl chloride and acetate.<sup>330</sup>

The polyvinyl esters have relatively good adhesion to metals. This has been utilized in the preparation of molds for thermoplastic materials. The mold of vinyl resin was coated by spraying the metal on it. If the final coat consisted of a high-melting substance, a low-melting one (zinc or tin) was applied first.<sup>321</sup> A similar use is to interpose a layer of polyvinyl compound between a metal coating and another synthetic resin.<sup>323</sup> However, Groff states that in producing composite molded articles having both metallic and resinous portions the metallic portions should be sized with a cumarone or an alkyd resin in order to cause the polyvinyl compound to adhere.<sup>323</sup>

Not only the acetate, but any of the polyvinyl esters may be spun into artificial silk. The thread after it is formed is stretched in several stages.<sup>324</sup> For example, mixtures of polymerized vinyl esters, benzene, and plasticizers are extruded as threads, which are stretched while hot and cooled under tension.<sup>325</sup> Interpolymers of vinyl chloride (70-93 per cent) and vinyl acetate have been proposed

<sup>322</sup> S. E. Sheppard, U. S. P. 1,921,948, Aug. 8, 1933, to Eastman Kodak Co.; *Chem. Abs.*, 1933, 27, 5180.

<sup>323</sup> C. E. Greider, U. S. P. 1,786,205, Dec. 23, 1930, to National Carbon Co., Inc.; *Chem. Abs.*, 1931, 25, 567.

<sup>324</sup> A. F. Caprio, Canadian P. 314,576, 1931, to Celluloid Corp.; *Chem. Abs.*, 1931, 25, 5526. British P. 366,077, 1930; *Brit. Chem. Abs. B.*, 1932, 357.

<sup>325</sup> C. Dreyfus, U. S. P. 1,950,662, Mar. 13, 1934; *Chem. Abs.*, 1934, 28, 3548. British P. 308,587, 1929, to British Celanese, Ltd.; *Brit. Chem. Abs. B.*, 1930, 99.

<sup>327</sup> J. F. Walsh and A. F. Caprio, British P. 308,657, 1929, to Celluloid Corp.; *Chem. Abs.*, 1930, 24, 499.

<sup>328</sup> C. M. Saeger, Jr., U. S. P. 1,859,905, Dec. 6, 1932; *Chem. Abs.*, 1933, 27, 1727.

<sup>329</sup> British P. 408,502, 1933, to Siemens & Halske A.-G.; *Chem. Abs.*, 1934, 28, 3269.

<sup>330</sup> M. C. Reed, U. S. P. 1,939,346, Jan. 29, 1935, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1935, 29, 1903.

<sup>321</sup> British P. 360,743, 1931, to Celluloid Corp.; *Brit. Chem. Abs. B.*, 1932, 154.

<sup>322</sup> H. Schuhmann, German P. 556,634, 1930, to Allgem. Elektrizitäts-Ges.; *Chem. Abs.*, 1933, 27, 434. Allgem. Elektrizitäts-Ges., British P. 377,556, 1931, to Internat. Gen. Elec. Co., Inc.; *Brit. Chem. Abs. B.*, 1932, 948.

<sup>323</sup> F. Groff, British P. 392,776, 1933, to Carbide & Carbon Chemicals Corp.; *Chem. Abs.*, 1934, 28, 354.

<sup>324</sup> British P. 337,976, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4672. French P. 743,468, 1933; *Chem. Abs.*, 1933, 27, 5333. Apparatus for producing foils and threads from polyvinyl-resin solutions is described in British P. 344,488, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 7.

<sup>325</sup> British P. 419,530, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1935, 111.

for filaments and films.<sup>336</sup> The resin in acetone is extruded into a precipitating medium, removed under tension at such a rate that only a superficial film is formed, and dried. Sheets or threads made in this manner can be stabilized to a desired form or dimension by subjecting them to the action of heat or swelling agents and then cooling or drying.<sup>337</sup>

There are a number of applications of vinyl resins which do not fall into the categories of lacquers, adhesives and molding materials. For example, by dusting fusible polyvinyl resins over a printed page while the ink was yet damp and then heating, relief print has been produced.<sup>338</sup> Vinyl resins have also been used as plasticizing agents for alkyd resins<sup>339</sup> and as stabilizing agents in suspensions of synthetic resins in organic liquids.<sup>340</sup> Branchen<sup>341</sup> has described a method for recovering both the cellulose ester and vinyl resin from scrap sheeting material, the vinyl resin being extracted with 1,2-dichloropropane. An oil-soluble dyestuff has been prepared by coupling diazotized p-nitroaniline with vinyl resins.<sup>342</sup> Dispersions of vinyl resins have been used to deluster rayon.<sup>343</sup> The chewing gum named "Chex" contains a vinyl resin and sulphur as two of the ingredients.<sup>344</sup> Another chewing gum base has been made by adding an equal weight of masticated crepe rubber to polyvinyl chloride while the latter was being treated in a roll mill.<sup>345</sup>

<sup>336</sup> H. F. Robertson, British P. 418,550, 1934, to Carbide & Carbon Chemicals Corp.; *Brit. Chem. Abs.*, B, 1935, 18. French P. 767,093, 1934; *Chem. Abs.*, 1935, 29, 254.

<sup>337</sup> H. E. Renard, French P. 765,181, 1934; *Chem. Abs.*, 1934, 28, 6956.

<sup>338</sup> German P. 574,389, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3790.

<sup>339</sup> French P. 733,836, 1932, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 27, 1221.

<sup>340</sup> German P. 592,310, 1934, to Allgem. Elektrizitäts-Ges.; *Chem. Abs.*, 1934, 28, 2928.

<sup>341</sup> L. E. Branchen, U. S. P. 1,964,191, June 26, 1934, one-half each to Carbide & Carbon Chemicals Corp. and Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 3236.

<sup>342</sup> H. Plauson, U. S. P. 1,500,844, July 8, 1924; *Chem. Abs.*, 1925, 19, 186.

<sup>343</sup> French P. 762,899, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5255. See also G. Schwen and H. Fikentscher, German P. 602,758, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 944.

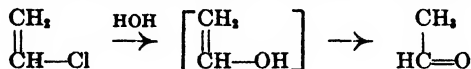
<sup>344</sup> Private communication from G. J. Manson.

<sup>345</sup> M. C. Reed, U. S. P. 1,989,246, Jan. 29, 1935, to Carbide & Carbon Chemicals Corp.

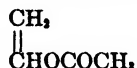
## Chapter 52

### Polyvinyl Alcohol. Polyvinyl Acetals

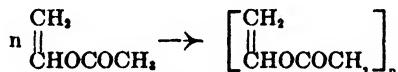
Vinyl alcohol has not been isolated; polyvinyl alcohol is the only form in which it is known. The simple alcohol should be formed by the hydrolysis of monochloroethylene but this reaction yields the isomeric acetaldehyde.



These two substances represent the keto and enol forms, of which the keto form (acetaldehyde) is the stable one. Although the enolic form (vinyl alcohol) is unknown, the acetylated compound is capable of existence as vinyl acetate:

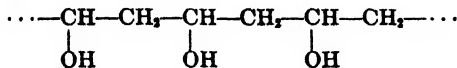


Polyvinyl alcohol has to be prepared indirectly and this is accomplished through polyvinyl acetate. Under the influence of catalysts and light, vinyl acetate yields polyvinyl acetate:

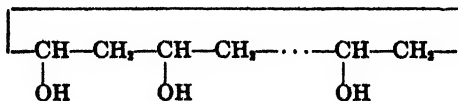


where  $n$  may vary between 20 and 900.<sup>1</sup> Hydrolysis of polyvinyl acetate with either alkali or acid yields a mixture of polyvinyl alcohols which are insoluble in benzene and chloroform. The simpler alcohols form colloidal solutions in cold water, formamide, ethylene glycol and glycerol. The more complex derivatives can be dispersed in these solvents by heat. The solubility of the polyvinyl alcohols suggests the behavior of starch. The essential difference between the two types of compounds is that the polyvinyl alcohols are much more stable<sup>2</sup> and do not yield monomeric units by hydrolytic cleavage.

On the basis of evidence from other linear polymers<sup>3</sup> the structure of polyvinyl alcohol can be considered to be



Another structural formula suggested<sup>4</sup> is of the cyclic type:



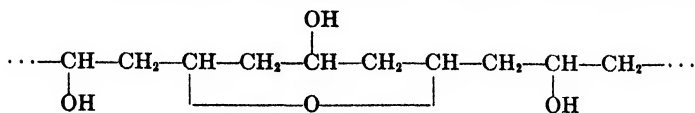
<sup>1</sup> H. Staudinger and A. Schwalbach, *Ann.*, 1931, 488, 8; *Brit. Chem. Abs. A*, 1931, 1032.

<sup>2</sup> H. Staudinger, K. Frey and W. Starck, *Ber.*, 1927, 60, 1782; *Brit. Chem. Abs. A*, 1927, 1051.

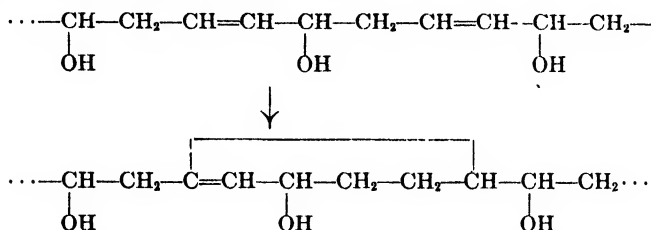
<sup>3</sup> H. Staudinger, "Hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932, 40. See Chapter 4.

<sup>4</sup> H. Staudinger, K. Frey and W. Starck, *loc. cit.*

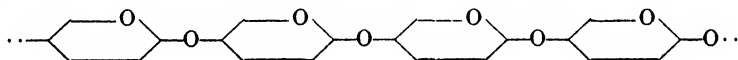
There is also the possibility of the formation of smaller rings by etherification:



or by dehydration followed by cyclization:



The alcohol groups retain their reactivity in the macromolecule and may be acetylated or benzoyleated. Neither procedure, however, can be carried to completion; in other words, the acetylation of polyvinyl alcohol will not yield as completely an acetylated compound as is the polyvinyl acetate obtained by polymerizing vinyl acetate. The methyl ether prepared from polyvinyl alcohol resembles methylated starch. Attention has already been called to the marked similarity of solubility behavior of starch and polyvinyl alcohol. The parallelism may be carried further by comparing the 6-membered ring structures of polyvinyl alcohol shown above with the conventional formula for starch:



#### PREPARATION OF POLYVINYL ALCOHOL

As mentioned previously, polyvinyl alcohol is prepared from its polymeric esters by hydrolysis with acid or alkali.<sup>5</sup> A uniformly light yellow or brown product results with caustic saponification. When acid is used, the nature of the original substance determines the color and density of the final product, which may vary widely. Acid hydrolysis is carried out by passing hydrogen chloride into a boiling alcoholic solution of the ester or by boiling the alcoholic solution for several hours with a little sulphuric acid.<sup>6</sup> Langenbeck and Baltes<sup>7</sup> have investigated the effect of catalysts upon the hydrolysis of polyvinyl acetate. For their work 1.7 g. (0.002 mol) of a 10 per cent solution of polyvinyl acetate was dissolved in quinoline along with 3 cc. of a 1 per cent solution of potassium acetate dissolved in isopropyl alcohol. The quantity of catalyst varied from 0.002 to 0.01 mol. The solutions were sealed in glass tubes and heated in the vapor from boiling cyclohexanol (approximately 160°C.). The extent of hydrolysis was determined by saponifying the resulting distillate of isopropyl acetate with 0.1 *N* barium hydroxide solution. The results obtained are given in Table 55 (on page 1056). Polyvinyl alcohol can be separated from its compounds by extraction with anhydrous mono- or polyhydric alcohols, using an acid or basic saponification catalyst.<sup>8</sup>

<sup>5</sup> W. O. Herrmann and W. Haehnel, *Ber.*, 1927, 60, 1658; *Chem. Abs.*, 1928, 22, 214.

<sup>6</sup> A. Skrabal and A. Lahorka (*Monatsh.*, 1927, 48, 459; *Brit. Chem. Abs. A*, 1927, 1148) have studied the kinetics of the hydrolysis of freshly prepared unimolecular vinyl acetate and find that the velocity of hydrolysis is much more rapid than in the case of ethyl acetate.

<sup>7</sup> W. Langenbeck and J. Baltes, *Ber.*, 1934, 67, 387; *Chem. Abs.*, 1934, 28, 3379.

<sup>8</sup> French P. 766,103, 1934, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 7261.

TABLE 55.—Catalytic Hydrolysis of Polyvinyl Acetate.

Catalysts	Quantity of Catalyst in Mols	Reaction Time in Hours	Volume of 0.1N Ba(OH) <sub>2</sub> in cc.	
			With Catalyst	Without Catalyst
Benzyl alcohol . . . . .	0.01	10	4.55	2.21
Naphthylcarbinol . . . .	0.005	15	4.92	3.00
Glycolanilide . . . . .	0.002	15	7.40	3.00
Benzoylcarbinol . . . .	0.002	15	5.02	2.26

Herrmann and Haehnel<sup>9</sup> stated that polyvinyl alcohol behaves like a typical reversible colloid. The fact that it can be purified by dialysis helps to confirm the colloidal explanation. This alcohol would have to function chiefly as a hydrosol since it is insoluble in almost all other substances. In contradistinction to gelatin it swells only slightly in water and dissolves readily at ordinary temperatures. With hot glycerol or glycol, polyvinyl alcohol gives a clear solution that gelatinizes on cooling. The alcohol in phenol, however, remains liquid on cooling if there is a trace of water present. With dispersoids, e.g., metals, oxides, hydroxides and sulphides, polyvinyl alcohol acts as a protective colloid. Its molecular weight was estimated to be 868 by the osmotic method. The acetylation reaction: polyvinyl alcohol → polyvinyl acetate, is accomplished by pressure and heat. On heating polyvinyl alcohol to 200–220°C. under 30 atmospheres pressure, it forms a hard, horny mass which is less soluble in glycerol, glycol and water than the original polymer, and more soluble in hot linseed and castor oils. Acetylation of this solid product results in the formation of typical polymeric vinyl acetate.

Polyvinyl alcohol will, according to Herrmann and Haehnel,<sup>10</sup> react with bromine to form addition compounds, which are converted by boiling water into a black insoluble form of the alcohol. A similar addition reaction occurs with chlorine. It is stated that the alcohol cannot be oxidized by potassium permanganate or by chromium trioxide, though oxidation with nitric acid gives oxalic acid. With benzaldehyde, polyvinyl alcohol reacts to form an acetal, and with formaldehyde, compounds allied to amyloform of starch (amyloextrin treated with formaldehyde) are obtained. The latter substances are somewhat more elastic than amyloform, are insoluble and do not swell in water, are fusible, and are more stable towards heat. When treated with dilute acids and alkalis they slowly lose formaldehyde. The aldehyde derivatives have attained some industrial significance, and will be discussed later. The polyvinyl alcohols resemble crude rubber in that they can be vulcanized with sulphur, the addition of accelerators being optional. Cold vulcanization gives soft gum-like substances which are elastic, and hot vulcanization yields a hard black mass which can be readily worked.

The method of Herrmann and Haehnel for converting polyvinyl acetate into polyvinyl alcohol, as already described, may be applied to production on a large scale.<sup>11</sup> The polymer of vinyl alcohol is obtained as an odorless, white, water-soluble powder. By evaporating a water solution of the polymer, films or thin sheets of high elasticity and strength may be obtained. Polyvinyl alcohol is also formed in the saponification of polyvinyl halides. Thus, from polyvinyl chloride with sodium hydroxide in the presence of light, and using uranyl nitrate as a catalyst, a 90 per cent yield of the alcohol is obtained.<sup>12</sup> According to Noller<sup>13</sup>

<sup>9</sup> W. O. Herrmann and W. Haehnel, *Ber.*, 1927, 60, 1658; *Chem. Abs.*, 1928, 22, 214.

<sup>10</sup> W. O. Herrmann and W. Haehnel, *loc. cit.*

<sup>11</sup> W. O. Herrmann and W. Haehnel, U. S. P. 1,672,156, June 5, 1928, to Consortium für elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs.* B, 1928, 665. Canadian P. 265,173, 1926; *Chem. Abs.*, 1927, 21, 918.

<sup>12</sup> W. Haehnel and W. O. Herrmann, German P. 516,996, 1932, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 3018.

<sup>13</sup> C. R. Noller, U. S. P. 1,897,356, Feb. 14, 1932, to Eastman Kodak Co.; *Chem. Abs.*, 1932, 27, 2096.



polymerized vinyl acetate may be saponified with an alkali metal hydroxide in presence of an alcohol, such as ethyl alcohol, and sufficient water to prevent precipitation of the polymerized product. The latter is subsequently precipitated by adding alcohol. By treating polymerized vinyl alcohol with butyric acid anhydride a neutral butyrate results, which is a rubber-like, alcohol-soluble substance, from which elastic threads or membranes may be produced. When polymerized vinyl alcohol is melted with an equivalent quantity of aleuritic acid or trihydroxystearic acid, an aleuritinate or trihydroxystearate is obtained. Both of these substances are very hard, elastic and practically insoluble in most solvents. Herrmann and Haehnel<sup>14</sup> have also described vinyl glycolate, which is soluble in ammonia and in pyridine.

The polymerization of the vinyl esters,<sup>15</sup> which forms the first step in the production of the alcohols, can be carried out at 40-160°C. in the presence of a compound such as barium peroxide, benzoyl peroxide, percarbonates, persulphates, or perborates, together with organic acid anhydrides, but without solvents or diluents. Under such conditions the product is practically insoluble in ethyl acetate, alcohol or acetone. Saponification gives a water-soluble vinyl alcohol, the viscous water solutions of which are useful as dispersing media for dye pastes, sizing or dressing compositions.<sup>16</sup> The hydrolysis may be carried out with ethyl alcohol and sulphuric acid.

Klatte and Müller<sup>17</sup> employed ammonium hydroxide for the saponification of polyvinyl mixed esters. Polyvinyl acetate-chloroacetate, for example, with ammonium hydroxide gave a solid polyvinyl alcohol. Partial or complete saponification of the mixed polymerization products obtained by the co-polymerization of vinyl halides with styrene, butadiene or acrylic ester, or of acrylic ester with vinyl acetate<sup>18</sup> also yields substances having some of the properties of polyvinyl alcohols.<sup>19</sup> Products of high viscosity are formed by the addition of a boron compound, e.g., an ester of boric acid, fluoboric acid, or acetofluoboric acid, to polymerized vinyl alcohol, the mixture being maintained in a neutral or slightly alkaline condition. In place of polyvinyl alcohol itself, vinyl alcohol which has been partly etherified or esterified may be used.<sup>20</sup>

#### USES OF POLYVINYL ALCOHOL

Polyvinyl alcohol may be employed for the production of resists (preparations which prevent dyes from adhering to fabrics) under vat colors. The fabric is printed with an oxidant, such as sodium m-nitrobenzenesulphonate or sodium dichromate, and an aqueous solution of a polyvinyl alcohol. It is then dried and dyed with the vat dye. The polyvinyl alcohol is coagulated in the warm vat, and adheres to the printed portions of the fabric.<sup>21</sup> In printing with vat dyes (which need alkali for fixing them on the fiber), a paste free from alkali and containing polymerized vinyl alcohol as the thickening-agent may be used. The prints are subsequently treated in an alkaline bath.<sup>22</sup> The alcohols of very high viscosity

<sup>14</sup> W. O. Herrmann and W. Haehnel, *loc. cit.*

<sup>15</sup> See Chapter 51.

<sup>16</sup> British P. 353,806, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5309. French P. 706,593, 1930; *Chem. Abs.*, 1932, 26, 154.

<sup>17</sup> F. Klatte and H. Müller, German P. 515,780, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3440. Cf. F. Klatte and A. Zimmermann, German P. 514,593, 1928; *Chem. Abs.*, 1931, 25, 2153.

<sup>18</sup> Cf. French P. 676,424, 1929, and 697,663, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 2846; 1931, 25, 3134.

<sup>19</sup> French P. 724,010, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4926.

<sup>20</sup> French P. 745,942, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4042.

<sup>21</sup> G. Torinus, U. S. P. 1,922,963, Aug. 15, 1933, to General Aniline Works; *Chem. Abs.*, 1933, 27, 5197. British P. 356,069, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 19. German P. 531,475, 1933; *Chem. Abs.*, 1931, 25, 5575.

<sup>22</sup> British P. 329,207, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 5510.

have found application in the sizing of fibers. Such polymers are obtained either by polymerizing the vinyl ester in the presence of a perborate and acetic anhydride and saponifying, or by the addition of a small quantity of borax to a polyvinyl alcohol of medium or low viscosity.<sup>22</sup>

Polyvinyl alcohols may be used in conjunction with other sizing agents and oils, fats, and waxes. Thus, an aqueous solution containing 0.2-0.33 per cent of sulphonated oil and 2-3.33 per cent of the alcohol is a representative sizing preparation. The size is equally suited for cotton, artificial silk or wool, and is readily removed by washing with warm water or 0.1-0.2 per cent soap solution.<sup>24</sup> Water-soluble derivatives of polyvinyl alcohol, including the products of the partial saponification of a polyvinyl ester, or those resulting from the condensation of an aldehyde and the alcohol, may be used instead of the polymerized alcohol itself.<sup>25</sup> For example, a fabric can be impregnated with a polyvinyl ester in an organic solvent. On drying, the fabric is treated with alkali or acid to produce complete or partial hydrolysis of the ester.<sup>26</sup>

Rayon or cotton may be sized with polyvinyl alcohol solutions having a viscosity 10 to 25 times that of an aqueous glycerol solution of equal concentration.<sup>27</sup> For sizing rayon, the incorporation of substances, e.g., fats, waxes or fatty acids, that reduce the adhesiveness of the aqueous alcohol solution, has been suggested.<sup>28</sup>

Jordan<sup>29</sup> prepared a composition for the coating of porous surfaces by emulsifying solutions of cellulose nitrate or acetate with an aqueous solution of polyvinyl alcohol.

A solution of polymerized vinyl alcohol in water serves as a stabilizer for hydrosols containing metals, metallic oxides or metallic sulphides.<sup>30</sup> The partially saponified polymerization products of vinyl acetate, dissolved in an anhydrous solvent, may be utilized as a binding medium in the production of plaster surgical bandages,<sup>31</sup> including those impregnated with plaster of Paris and other substances which set in water.

Relatively concentrated solutions of polyvinyl alcohols in water can be extruded through an orifice at raised temperatures and allowed to solidify to threads or ribbons. Fillers may be added, and the resistance of the product to water is believed to be improved by the incorporation of hydrophobic substances or by treatment with formaldehyde vapor at an elevated temperature.<sup>32</sup> The addition of a volatile organic liquid not itself a solvent for polyvinyl alcohol, such as ethyl alcohol, which promotes rapid evaporation of water, improves the uniformity of threads and tubes made in the above process.<sup>33</sup> Threads, so prepared, are said to be adaptable for medicinal and surgical use. The incorporation of 5-10 per cent of oxalic, malic or lactic acid in the polyvinyl alcohol surgical sutures is reported

<sup>22</sup> French P. 41,010, 1913, addn. to 687,155, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1523. British P. 332,735, 1931, addn. to 345,207; *Brit. Chem. Abs. B*, 1933, 16. Cf. French P. 41,138, 1933, addn. to 687,155; *Chem. Abs.*, 1934, 28, 656.

<sup>24</sup> British P. 345,207, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 535. British P. 399,905, 1933; *Chem. Abs.*, 1934, 28, 1874.

<sup>25</sup> British P. 372,599, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 722.

<sup>26</sup> E. Baum and W. O. Herrmann, German P. 595,375, 1934, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 4251.

<sup>27</sup> K. Jochum, A. Voss, H. Geier and E. Dickhäuser, U. S. P. 1,920,564, Aug. 1, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4937.

<sup>28</sup> German P. 646,081, 1934, to Firma L. Blumer; *Chem. Abs.*, 1935, 29, 1662.

<sup>29</sup> O. Jordan, German P. 565,267, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1215. British P. 334,567, 1929; *Chem. Abs.*, 1931, 25, 1108.

<sup>30</sup> W. O. Herrmann and W. Haehnel, U. S. P. 1,629,161, May 17, 1927, to Consortium für elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B*, 1927, 624. Canadian P. 266,717, 1926; *Chem. Abs.*, 1927, 21, 995.

<sup>31</sup> A. Eichengrün, British P. 335,658, 1930; *Chem. Abs.*, 1933, 27, 3295.

<sup>32</sup> British P. 356,161, 1932, to Consortium für elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 288. French P. 732,834, 1932; *Chem. Abs.*, 1933, 27, 416.

<sup>33</sup> British P. 399,493 and 399,505, 1932, to Consortium für elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 677.

to increase their capacity for being resorbed.<sup>44</sup> Polyvinyl alcohol has also been applied in the manufacture of photographic films. The rear side of a transparent cellulose film or glass plate emulsion support is coated with a layer of the alcohol containing an antihalation dye, which will act as a desensitizer in solution.<sup>45</sup>

A product stated to be useful for the manufacture of films and molded articles may be prepared by heating polyvinyl alcohol to 160°C. in order to render it water-insoluble. The heat treatment may be dispensed with in this conversion by using reagents capable of precipitating albumins, such as tannin or formaldehyde.<sup>46</sup>

### POLYVINYL ESTERS

Mixed esters of polyvinyl alcohol are formed by treating the polymerized alcohol with two or more acid halides, either together or in succession, and in the presence of an organic diluent and a tertiary base of the pyridine type. Compounds prepared in this manner may be used in the production of films, filaments, lacquers and coatings.<sup>47</sup> The mixed esters may be converted to an insoluble form by long heat treatment. As an example of this procedure, a mixture of polyvinyl alcohol, ethyl chloride, naphthenic acid chloride, chlorobenzene and pyridine bases may be heated to 35-40°C. for 24 hours. The ester is separated by treating the crude solution with methyl alcohol and filtering. It is used in acetone solution.

The partial hydrolysis of polyvinyl esters gives products which are employed as sizes or impregnating agents for textiles. Such a reaction occurs on heating polyvinyl acetate (with 90 per cent acetic acid containing sulphuric acid) at 40-60°C. until the polymer is soluble in 30-50 per cent aqueous ethyl alcohol. Another method for preparing compounds, which may be dissolved or dispersed in water, involves the esterification of polyvinyl alcohol with various acids such as lactic, tartaric, citric, malic, oxalic and maleic.<sup>48</sup> Voss and Starck<sup>49</sup> have reported that polymerized vinyl alcohol can be partially esterified to yield compounds soluble in organic solvents. The process, however, could not be utilized to produce water-insoluble esters. The extent of esterification is dependent upon the molecular weight of the acid radical, the maximum being obtained with acids of low molecular weight.

Polymerized vinyl acetate may be prepared directly from the polymerized alcohol by heating a solution of the latter in acetic anhydride with dry sodium acetate. An elastic mass of partially butylated polymerized vinyl alcohol is obtained on heating the alcohol with butyric acid.<sup>50</sup>

Combinations of polyvinyl esters and fatty oils are made by polymerizing vinyl esters in the presence of a polymerized fatty oil, usually in its "low-disperse phase." This phase is obtained by removing the non-polymerized portion with an aliphatic alcohol (propyl or higher) or an ester such as ethyl malonate. Oil varnishes, coating compositions, adhesives and plastics are made from these products.<sup>41</sup> A writ-

<sup>42</sup> British P. 420,052, 1933, addn. to 386,161 and 393,505, to Consortium für elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 112.

<sup>43</sup> S. E. Sheppard and J. G. McNally, U. S. P. 1,768,795, July 1, 1930; *Chem. Abs.*, 1930, 24, 4474.

<sup>44</sup> A. Voss, German P. 526,497, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 173.

<sup>45</sup> German P. 534,213, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 735. French P. 693,816, 1930; *Chem. Abs.*, 1931, 25, 1537.

<sup>46</sup> H. Dreyfus, British P. 335,978 and 396,005, 1931; *Brit. Chem. Abs. B*, 1933, 217. French P. 733,463, 1933; *Chem. Abs.*, 1933, 27, 1212.

<sup>47</sup> A. Voss and W. Starck, German P. 577,384, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3946.

<sup>48</sup> W. Haehnel and W. O. Herrmann, German P. 480,868, 1924, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1929, 23, 4951.

<sup>49</sup> A. Eibner, British P. 367,103, 1929, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 3053. See Chapter 61.

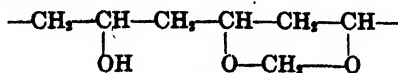
ing ink is prepared using a polyvinyl alcohol and a fatty oil to which pigments are added. White ink is made by incorporating zinc oxide.<sup>43</sup> Hydroxyalkyl and alkyl polyvinyl ethers are formed by the interaction of an alkylene oxide with a polyvinyl alcohol. The reaction is carried out under high pressure in the presence of inert gases, with the addition of such basic accelerators as dimethylaniline, trimethylamine, pyridine or alkalis. Thus, a polyvinyl alcohol prepared by the saponification of a polymerized vinyl acetate of high viscosity may be treated with ethylene oxide. Substituted polymers of this type may find application as thickening, dressing and sizing agents, and as plastics.<sup>44</sup>

#### VULCANIZED PRODUCTS FROM POLYVINYL COMPOUNDS

The treatment of polymerized vinyl alcohol or its derivatives with sulphur or sulphur compounds, as stated previously, leads to a reaction simulating the vulcanization of rubber. The properties of the product resemble the different qualities of soft and hard rubber according to the starting materials and the reaction conditions.<sup>45</sup> If polymeric vinyl alcohol is mixed with 1 per cent of sulphur and heated for 5 hours at 150°C. under a pressure of 10 atmospheres, there results a black, hard rubber-like material which can be worked by cutting, sawing or filing. A similar substance is formed by heating the alcohol with 2 per cent of sulphur and 2 per cent of piperidine as an accelerator for half an hour at 120°C. under 10 atmospheres pressure. Vulcanization can also be effected by covering polymerized vinyl alcohol at ordinary temperatures with a 10 per cent solution of sulphur monochloride in carbon disulphide. At the end of 24 hours, the crude resin is washed, giving a gray-colored plastic mass resembling vulcanized soft rubber. This process may also be carried out with the addition of fillers. For example, a mixture of polymeric vinyl alcohol, 25 per cent of ground slate and 1 per cent of sulphur was pressed for half an hour at 150°C. under a pressure of 100 atmospheres to yield a hard, slate-blue material.

#### CONDENSATION OF POLYVINYL ALCOHOLS WITH ALDEHYDES

The interaction of polymerized vinyl alcohol (derived from vinyl esters) with aldehydes furnishes a further group of substances which are of value as synthetic resins. Condensation products of rubber-like, plastic and elastic, or of hard and brittle character are obtained from alcohol and aliphatic aldehydes (e.g., formaldehyde, acetaldehyde).<sup>46</sup> (See Fig. 139.) An acid catalyst (e.g., zinc chloride, aluminum chloride, mineral acids) is used. It is also said that the use of a water-insoluble solvent (e.g., benzene) materially increases the yield.<sup>47</sup> Condensation probably occurs with elimination of water between the hydroxyl groups in the alcohol and oxygen in the aldehyde, giving an acetal grouping of the type shown below in the case where formaldehyde is employed.



<sup>43</sup> W. Haehnel and W. O. Herrmann, German P. 591,979, 1934, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 3926.

<sup>44</sup> A. Schmidt, G. Balle and K. Eisefeld, U. S. P. 1,971,662, Aug. 29, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6444. German P. 875,141, 1933; *Chem. Abs.*, 1933, 27, 3483. British P. 361,691, 1931; *Chem. Abs.*, 1933, 27, 1208. British P. 364,323, 1930; *Brit. Chem. Abs. B.*, 1932, 495. French P. 708,236, 1930; *Chem. Abs.*, 1933, 26, 1077. British P. 368,530, 1930; *Chem. Abs.*, 1933, 27, 2159.

<sup>45</sup> W. O. Herrmann and W. Haehnel, U. S. P. 1,672,157, June 5, 1928, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1928, 22, 3686.

<sup>46</sup> G. E. Ziegler, French P. 799,011, 1934; *Chem. Abs.*, 1935, 29, 526.

<sup>47</sup> British P. 368,730, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1934, 311. French P. 733,216, 1933; *Chem. Abs.*, 1934, 28, 1860.

The viscosity and solubility of the reaction product are dependent upon the quantity of acid employed.<sup>47</sup> The polymeric compounds may be vulcanized to hard substances resembling ebonite. This subsequent vulcanization is especially beneficial if unsaturated aldehydes such as acrolein have been used.<sup>48</sup>

The polyvinyl alcohol-aldehyde condensation may be carried out in such a way that the product is liquid and soluble in water. The essential conditions for water-solubility are the use of the minimum proportion of aldehyde and the avoidance of high temperatures.<sup>49</sup> Formalin used at its boiling temperature gives insoluble solid resins. With less reactive aldehydes such as benzaldehyde, aldol, butyraldehyde or glyoxal, larger proportions of the aldehyde and higher reaction temperatures may be utilized without forming solid products. The actual working conditions are indicated by the following examples:

Twenty parts of a polyvinyl alcohol of low viscosity are dissolved in 80 parts of water containing 2-3 per cent of sulphuric acid, and 25 parts of 30 per cent formaldehyde are added. The solution is kept at 60-65°C. until its viscosity has increased by at

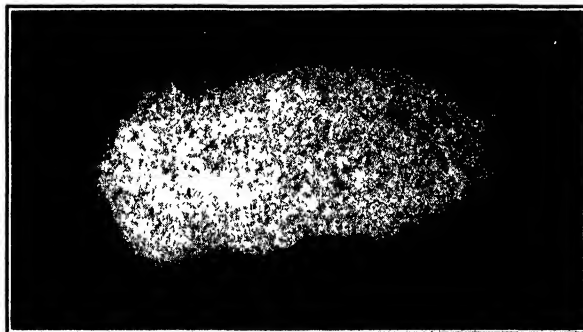


FIG. 139.—Acetal of Vinyl Alcohol in Flaky Form.

least 100 per cent. The reaction solution may then be used directly for manufacturing emulsions of insoluble dyestuffs, for sizing, dressing or for printing. Alternatively, the reaction product may be isolated by precipitating it with alcohol, filtering by suction, washing and drying. In the case of benzaldehyde, 150 parts of 12 per cent aqueous polyvinyl alcohol are mixed with 20 parts of the aldehyde. The mixture is heated on a water bath until a test sample solidifies in the cold to a gelatinous mass. The polymeric derivative under these conditions is soluble in water, the solutions being, as before, considerably more viscous than those of the alcohol itself. Any excess of aldehyde in the above reactions may be removed by the addition of ammonium hydroxide. An acid catalyst may also be used. For example, 125 parts of a 25 per cent aqueous solution of polyvinyl alcohol are mixed with 15 parts of acetaldehyde and 1 part of concentrated hydrochloric acid. The resulting mixture is heated on a water bath until a test sample shows the desired viscosity, whereupon the heating is discontinued and the free acid neutralized.

In a similar procedure, Belloc<sup>50</sup> obtained a condensation product, without the isolation of polyvinyl alcohol, by combining polymerized vinyl esters with an aldehyde in hydrochloric acid. Condensation may, also, be carried out in an anhydrous medium to yield polymers recommended as substitutes for celluloid in the

<sup>47</sup> G. E. Zelger, French P. 769,010, 1934; *Chem. Abs.*, 1935, 29, 528.

<sup>48</sup> W. Haehnelt and W. O. Herrmann, German P. 507,962, 1927, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1931, 25, 835. French P. 695,800 and 696,008, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2822, 2878. British P. 337,806, 1929; *Brit. Chem. Abs. B*, 1931, 170.

<sup>49</sup> British P. 356,408, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4481. French P. 699,676, 1930; *Chem. Abs.*, 1931, 25, 3499.

<sup>50</sup> M. Belloc, U. S. P. 1,990,599, Feb. 3, 1935, to Soc. Nobel française; *Chem. Abs.*, 1935, 29, 1906.

manufacture of lacquers.<sup>51</sup> The general procedure may be illustrated by the reaction between polyvinyl alcohol and acetaldehyde, in which phosphoric acid is the condensing agent and methylene chloride is the solvent. The mixture is boiled and the water formed distills over with the methylene chloride. Hopff and Kuehn<sup>52</sup> have used aldehydes in other forms, including trioxymethylene, metaldehyde and methylal. Polyhydric alcohols, such as those made by reducing polymeric methyl vinyl ketone, polymeric acraldehyde, or by hydrolyzing polymeric methyl vinyl acetates may be condensed with aldehydes in the same way as vinyl alcohol itself.<sup>53</sup> The vinyl alcohol-aldehyde condensation products already described<sup>54</sup> may be dissolved in organic solvents, such as chlorinated hydrocarbons, glycol ethers, esters, alcohols, hydrocarbons, and used in the preparation of lacquers, coating compositions, adhesives, impregnating solutions and for making films. The solutions may contain dyes or pigments.<sup>55</sup>

In a method employed by Zelger,<sup>56</sup> powders, grains, filaments, films, plates, tubes and other diversified forms in which polyvinyl alcohol-aldehyde condensation products can be obtained, are shaped to their ultimate external state before undergoing aldehyde condensation.

A modified polyvinyl acetal has been recommended by Voss, Dickhäuser and Starck<sup>57</sup> for the manufacture of molded articles. The acetal is prepared by condensing a mixed polymerization product of vinyl acetate and vinyl oleate with butyraldehyde. Condensation products from polyvinyl alcohols and aldehydes may also be used as celluloid substitutes, and for the manufacture of sound records.<sup>58</sup> For example, Schmidt<sup>59</sup> has described such a record possessing the requisite qualities of strength, toughness and durability. For its preparation, 50 kg. of a polyvinyl alcohol-formaldehyde condensation product were kneaded with 50 kg. of a 2:1 mixture of alcohol and benzene, along with 2.5 kg. of the isobutyl ester of phthalic acid as a plasticizing agent. This mass may subsequently be molded with heat and pressure. Another molding composition, suggested for sound records, consists of one or more polyvinyl ester-aldehyde hydrolytic products combined with an ester wax or a metallic stearate as lubricant. Fillers, pigments, resins and plasticizers may be added.<sup>60</sup>

Furthermore, polyvinyl acetals, when used in conjunction with cellulose solutions of the viscose type, are stated to improve the mechanical properties and to impart enhanced gloss, durability and softness to artificial threads made there-

<sup>51</sup> British P. 403,750, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3416.

<sup>52</sup> H. Hopff and E. Kuehn, U. S. P. 1,955,068, Apr. 17, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3936.

<sup>53</sup> British P. 369,313, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 475. I. Tanasescu and E. Macovski (*Bull. soc. chim.*, 1933, 53, 1097; *Chem. Abs.*, 1934, 28, 1330) have found that the product derived by treating dulcitol with o-nitrobenzaldehyde undergoes photochemical polymerization to yield resinous substances. P. Thomas and M. Sibi (*Compt. rend.*, 1926, 182, 314; *Chem. Abs.*, 1926, 20, 1742) have observed that the acetal of sorbitol forms a jelly when a previously boiled aqueous solution is allowed to cool. A product usable for making laminated paper or cellulose acetate foil has been prepared by condensing glycol or glycerol with formalglycerol. (G. W. Seymour, U. S. P. 1,990,068, Feb. 5, 1935, to Celanese Corp.; *Chem. Abs.*, 1935, 29, 1907.)

<sup>54</sup> Cf. British P. 337,306, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 170.

<sup>55</sup> British P. 373,603, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4106. French P. 719,667, 1931; *Chem. Abs.*, 1932, 26, 3943.

<sup>56</sup> G. E. Zelger, French P. 762,711, 1934; *Chem. Abs.*, 1934, 28, 5191.

<sup>57</sup> A. Voss, E. Dickhäuser and W. Starck, U. S. P. 1,939,422, Dec. 12, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1494. British P. 396,186, 1932; *Brit. Chem. Abs. B*, 1933, 905. German P. 592,333, 1934; *Chem. Abs.*, 1934, 28, 2859. A. Voss (German P. 473,171, 1927; to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 3113) condensed polyvinyl alcohol with a phenol-formaldehyde resin to produce insoluble and infusible substances.

<sup>58</sup> French P. 725,026, 1931, to Rheinisch-Westfälische Sprengstoff A.-G.; *Chem. Abs.*, 1932, 26, 4925. British P. 332,645, 1932; *Chem. Abs.*, 1932, 27, 4247. British P. 389,173, 1931; *Brit. Chem. Abs. B*, 1932, 399.

<sup>59</sup> F. Schmidt, U. S. P. 1,956,537, May 1, 1934; *Chem. Abs.*, 1934, 28, 4192.

<sup>60</sup> British P. 410,779, 1934, to Shawinigan Chemicals, Ltd.; *Chem. Abs.*, 1934, 28, 6337.

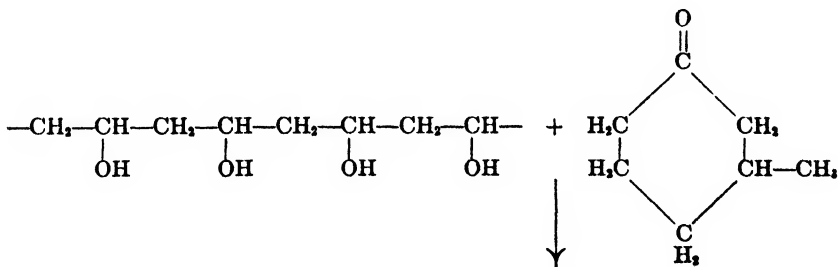
from.<sup>61</sup> A representative procedure involves the addition of sodium hydroxide, carbon disulphide and a solution of polyvinylformal in an organic solvent to a solution of cellulose xanthate. Filaments are formed and spun into threads according to the methods used in the viscose process. Another spinning-solution contains cellulose acetate dissolved in a mixture of methylene chloride and alcohol together with a polyvinyl acetal.<sup>62</sup>

The polyvinyl alcohol condensation with aldehydes may be further modified if a substance capable of condensing with the aldehyde is introduced into the reaction mixture. Such compounds as phenol, aromatic amines, urea, gelatin, or casein may be used for this purpose. The products vary from horn-like or moldable masses and lacquer-base resins to water-soluble products which are applied as emulsifiers and tanning agents. Mild reaction conditions yield viscous water-soluble products and prolonged heating gives resins which are insoluble in water.<sup>63</sup>

#### CONDENSATION OF POLYVINYL ALCOHOLS WITH KETONES

The action of condensing-catalysts on mixtures of polyvinyl alcohols (or esters) and cyclic ketones yields condensation products. When, for example, polyvinyl alcohol, ethyl alcohol, benzene and methylcyclohexanone are heated to 80°C. with concentrated sulphuric acid, a resin is obtained in the form of a white powder.<sup>64</sup> These resins are soluble in water and also in organic solvents. Cyclohexanone, its 4-chloro derivative and 1-keto-tetrahydronaphthalene are other examples of ketones available for this purpose.

The constitutions of these condensation products have not yet been fully ascertained. However Kränzlein, Voss and Starck<sup>65</sup> assumed that the union takes place by the loss of water in which the hydrogen atoms are furnished by hydroxyl groups of the alcohol and the oxygen by the ketone group. For example, the condensation between polyvinyl alcohol and 2-methylcyclohexanone may proceed according to the following equation:



(The assumed result of the reaction between polyvinyl alcohol and the cyclic ketone, 2-methylcyclohexanone, is indicated on the following page.)

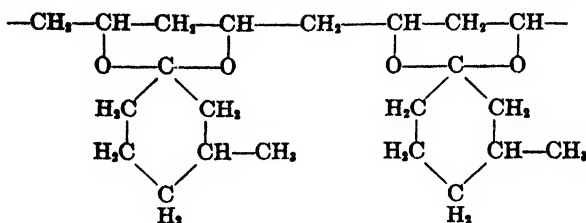
<sup>61</sup> A. Steindorff and G. Balle, German P. 574,970, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4673. British P. 372,647, 1932; *Chem. Abs.*, 1933, 27, 3605. Cf. French P. 751,824, 1932, to Soc. Nobel française; *Chem. Abs.*, 1934, 28, 895. See also M. Jeanny, Russia, 1934, 9, 99, 101, 175; *Chem. Abs.*, 1934, 28, 3237.

<sup>62</sup> British P. 367,374, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2033.

<sup>63</sup> A. Voss, German P. 543,286, 1929; to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2286. British P. 261,910, 1930; *Brit. Chem. Abs. B.*, 1932, 95. French P. 700,411, 1930; *Chem. Abs.*, 1931, 25, 3782.

<sup>64</sup> G. Kränzlein, A. Voss and W. Starck, German P. 551,968, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4837. British P. 233,764, 1931; *Chem. Abs.*, 1933, 27, 4247.

<sup>65</sup> G. Kränzlein, A. Voss and W. Starck, U. S. P. 1,933,996, Nov. 7, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 664.



## POLYMERIZATION PRODUCTS OF VINYL ESTERS WITH ALDEHYDES

Ordinarily reaction between vinyl esters and aldehydes is slow, but at high temperatures and pressures condensation proceeds readily. For example, 0.1 part of acetaldehyde and 100 parts by volume of vinyl acetate heated in a bomb for 16 hours at 100°C. yield 66 parts of a product which is hard when cold but tough and rubbery when warm.<sup>66</sup> Resins prepared with a larger proportion of aldehyde are gummy, semi-liquid, or liquid substances. With 10-15 parts of aldehyde per 100 parts of vinyl acetate, the product has the consistency of chewing gum and can be used in the manufacture of the latter.

Esters such as vinyl butyrate or formate, or esters of higher molecular weight, give results similar to those obtained with vinyl acetate. Vinyl ethers, vinyl halides or other compounds containing ethylene linkages may be substituted for the esters. Similarly formaldehyde, paraldehyde, butyraldehyde or aldehydes of higher molecular weight may be used in place of acetaldehyde. Compounds of the acetal type may be employed under conditions such that they will liberate acetaldehyde. The reaction is inhibited by sulphur and certain sulphur compounds, and is retarded by iron and copper and some of their compounds. Vessels constructed of these materials must therefore be avoided, and glass, porcelain, enamel or aluminum used in their place. The presence of oxygen was found, in general, to accelerate the reaction and improve the yield, but it is doubtful if it is essential. A small amount of a catalyst such as hydrogen chloride may be added to the reaction system.<sup>67</sup> This reaction was found to be greatly facilitated by illumination. The effective part of the spectrum lies in the visible range, and the reaction mixture may accordingly be contained in a vessel of Pyrex and subjected to the light of a mercury arc. Good yields of resin are obtainable in the illuminated systems without the use of heat and pressure.<sup>68</sup> In this case oxygen was found to have very little effect either on the speed of reaction or on the product.

Matheson and Skirrow noted a connection between exposure of vinyl esters to oxygen and the ease of polymerization. In general, the esters treated with oxygen and exposed to light were active, whereas esters from which oxygen had been excluded during manufacture were inactive and would not polymerize. The conditions required in the case of polymerization were found to apply also to the reaction of vinyl esters with aldehydes and acetals.<sup>69</sup>

Aldehyde-polyvinyl ester condensations are usually carried out in the presence

<sup>66</sup> H. W. Matheson and F. W. Skirrow, U. S. P. 1,752,362, Aug. 20, 1929, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1929, 23, 5051.

<sup>67</sup> F. W. Skirrow, British P. 250,240, 1927, to Canadian Electro Products Co., Ltd.; *Brit. Chem. Abs. B*, 1928, 144. British P. 295,533, 1928; *Brit. Chem. Abs. B*, 1930, 339. H. W. Matheson and F. W. Skirrow, Canadian P. 258,644, 1929; *Chem. Abs.*, 1929, 23, 3115. French P. 643,419, 1927, and 668,684, 1928; *Chem. Abs.*, 1928, 23, 1517, 5338. German P. 563,792, 1927; *Chem. Abs.*, 1933, 27, 1236.

<sup>68</sup> F. W. Skirrow, U. S. P. 1,746,618, Feb. 11, 1930, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1930, 24, 1754. Canadian P. 237,494, 1929; *Chem. Abs.*, 1929, 23, 1908.

<sup>69</sup> H. W. Matheson and F. W. Skirrow, U. S. P. 1,746,665, Feb. 11, 1930, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1930, 24, 1754.



of oxygen. It is also possible to use benzoyl peroxide in amounts varying between 0.01 and 1 per cent as a catalyst in the condensation reaction.<sup>76</sup> Leopold and Michael,<sup>77</sup> however, have obtained transparent to red resins by condensing a vinyl ester, such as the acetate, with aliphatic aldehydes or substances generating them, at temperatures of the order of 150°C. and pressures of 20 atmospheres. Para-formaldehyde and vinyl acetate under such conditions gave a yellow fusible resin. The absence of oxygen was emphasized as one of the conditions of this reaction. The products were said to be useful in the manufacture of spirit varnishes and polishes. The reaction of vinyl ester with acetaldehyde has also been carried out in the presence of toluene, the latter serving as a modifier for the reaction.<sup>78</sup>

Chewing gum can be manufactured from the condensation product of aliphatic vinyl esters and saturated aliphatic aldehydes by incorporating sugar and flavoring ingredients.<sup>79</sup> The condensation product used in the preparation of chewing gum is tasteless and insoluble in water or saliva, and is not as sticky as gum chicle. However, the synthetic resin possesses the desirable properties of gum chicle and does not harden on continued chewing. The derivative obtained from a polyvinyl ester and an aldehyde has been suggested for use in lacquers, varnishes, enamels and paints. The condensation product (presumably in the hard forms) is recommended as a substitute for shellac and other resinous binders.<sup>80</sup> Mixed with clay, rubber, sulphur, zinc oxide and coloring matter, it may also serve as a rubber substitute.<sup>81</sup> An emulsion, said to be adaptable for use in chewing gums, is prepared by heating a vinyl ester-aldehyde gum with a polyhydric alcohol such as ethylene glycol, cooling the mixture, and separating the resulting emulsion from the excess alcohol.<sup>82</sup>

The production of plastic materials by reaction between a polyvinyl ester in solution and an acetal has been reported.<sup>83</sup> The condensation is effected in absolute alcohol solution using hydrogen chloride as the condensing catalyst.

#### ALDEHYDE TREATMENT OF HYDROLYZED VINYL ESTER-ALDEHYDE PRODUCTS

Vinyl ester polymers and the vinyl ester-aldehyde products may be hydrolyzed by heating with dilute mineral acids and water to yield a gummy product.<sup>84</sup> Skirrow, Morrison and Blaikie<sup>85</sup> found that further condensations of these hydrolyzed or partially hydrolyzed materials with aldehydes yielded resinous substances which were, in general, harder and tougher than the gums from which they were formed. The exact nature of the product obtained in this manner depends on the amount and character of both the primary and the secondary aldehyde, the extent of

<sup>76</sup> F. W. Skirrow, U. S. P. 1,872,834, Aug. 3, 1932, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1932, 26, 5904. Canadian P. 311,483, 1931; *Chem. Abs.*, 1931, 25, 3448.

<sup>77</sup> R. Leopold and A. Michael, German P. 449,115, 1925, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1928, 867.

<sup>78</sup> K. G. Blaikie, G. O. Morrison and T. P. G. Shaw, Canadian P. 329,996, 1933, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1933, 27, 2159.

<sup>79</sup> H. W. Matheson, British P. 280,247, 1927, to Canadian Electro Products Co., Ltd.; *Brit. Chem. Abs. B*, 1929, 301. Canadian P. 289,983, 1929; *Chem. Abs.*, 1929, 23, 3543. German P. 563,792, 1927; *Chem. Abs.*, 1928, 27, 1236. German P. 553,914, 1933; *Chem. Abs.*, 1934, 28, 2230.

<sup>80</sup> H. W. Matheson, Canadian P. 288,641 and 288,642, 1929, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1929, 23, 3113, 3114.

<sup>81</sup> H. W. Matheson, Canadian P. 288,640, 1929, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1929, 23, 3376.

<sup>82</sup> K. G. Blaikie and G. O. Morrison, U. S. P. 1,906,207, Apr. 25, 1933, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1933, 27, 3570.

<sup>83</sup> D. T. Jones, A. Renfrew and R. Burns, British P. 404,379, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 3849.

<sup>84</sup> F. W. Skirrow and G. O. Morrison, U. S. P. 1,971,931, Aug. 28, 1934, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1934, 28, 6590. Canadian P. 318,645, 1933; *Chem. Abs.*, 1933, 26, 3071.

<sup>85</sup> F. W. Skirrow, G. O. Morrison and K. G. Blaikie, British P. 331,063, 1930, to Canadian Electro Products Co., Ltd.; *Brit. Chem. Abs. B*, 1931, 853. Canadian P. 318,644, 1933; *Chem. Abs.*, 1933, 26, 2673. French P. 692,715, 1930; *Chem. Abs.*, 1931, 25, 1093.

hydrolysis of the gum, and the nature and quantity of the acid catalyst used.<sup>80</sup> The following example illustrates the reaction conditions:

To 1000 parts by weight of the vinyl acetate-acetaldehyde gum (obtained by reacting vinyl acetate with 2.7 per cent of its weight of aldehyde) are added 2000 parts by weight of ethyl alcohol to form a solution. To this are added 450 parts of formalin solution and 25 parts of concentrated hydrochloric acid, and the whole allowed to react for 14 hours at approximately 100°C. in an autoclave. After recovery of the solvent and the ethyl acetate formed and removal of acid, the product is dried. The purified derivative is described as a molding resin which can be worked on hot rolls and mixed with the usual fillers.

The hydrolysis and secondary aldehyde reactions take place simultaneously. The hydrolysis proceeds to an extent of about 60 per cent as estimated by the total acid liberated, both free and as ethyl acetate. The use of less aldehyde in the primary condensation leads to a harder, tougher and stronger resin. Ethyl alcohol may be replaced by analogous solvents but its use has the advantage that the acetic acid is largely recovered as the ethyl ester.

The product of hydrolysis may be isolated if required, the whole operation being then conducted in two stages. Use of acetaldehyde in place of formaldehyde in the second stage of the condensation leads to substances which are less hard and tough. The primary gum-like product may be made with aliphatic vinyl esters other than vinyl acetate, and with various aldehydes. Thus, vinyl butyrate or propionate, butyraldehyde, propylaldehyde and other compounds of the same series all give similar results. The primary condensation products utilized in these reactions do not lend themselves to the manufacture of molding resins, since they lack physical strength and toughness, and have softening points which are generally too low.

Starting with a definite primary gum-like product the characteristics of the secondary aldehyde resins vary widely. Those resulting from limited hydrolysis are of low softening point which increases as the percentage hydrolysis is increased. The product of complete hydrolysis of the primary gum when condensed with an aldehyde gives a resin of very high softening point. The resins may be used either in the pure state or blended.

A polyvinyl resin (made by hydrolysis of the ester and reaction with an aldehyde) is employed in a composition for injection molding. Impact-strength promoters, lubricants, fillers and pigments are added.<sup>81</sup> This resin can be used for phonograph records<sup>82</sup> and for paints, varnishes and enamels<sup>83</sup> by the addition of necessary modifying constituents. Schmidt<sup>84</sup> prepared a celluloid substitute by kneading a polyvinyl alcohol-formaldehyde condensation product (100 kg.) with alcohol (60 l.) and benzene (30 l.) at 30°C. The major portion of the solvent was driven off on hot rolls, and the mass was compacted at 80°C. under a pressure of 20 kg. per sq.cm. The resulting block was cut into foils, dried and polished.

Saponification of the polymerization product of vinyl acetate and maleic anhydride, followed by heating of the product with formaldehyde, gives a material which is recommended for making resistant lacquers.<sup>85</sup>

Plastic materials are obtained by reacting a polyvinyl ester with ethylidene diacetate, in the presence of anhydrous alcohol and an acid catalyst. They may be

<sup>80</sup> F. W. Skirrow and G. O. Morrison, U. S. P. 1,971,951, Aug. 28, 1934, to Canadian Electro Products Co., Ltd.; *Chem. Abs.*, 1934, 28, 6588.

<sup>81</sup> British P. 410,506, 1934, to Shawinigan Chemicals, Ltd.; *Chem. Abs.*, 1934, 28, 6580.

<sup>82</sup> British P. 410,776, 1932, to Shawinigan Chemicals, Ltd.; *Brit. Chem. Abs.* B, 1934, 696.

<sup>83</sup> F. W. Skirrow and S. Whyte, British P. 405,986, 1934; *Chem. Abs.*, 1934, 28, 4922.

<sup>84</sup> F. Schmidt, U. S. P. 1,966,216, April 2, 1935.

<sup>85</sup> French P. 737,744, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1773.

employed in the preparation of lacquers, varnishes, enamels, shellac substitutes (in record manufacture) and molded articles.<sup>60</sup>

### MISCELLANEOUS PRODUCTS

The polymerization of a mixture of a vinyl halide with less than 43 per cent by weight of a vinyl compound containing oxygen, e.g., the acetate, in presence of benzoyl peroxide and a stabilizer (calcium stearate or titanium oxide) yields a uniform moldable resin.<sup>61</sup> It is advocated for the manufacture of sound records, and floor or wall surfaces. After the incorporation of large amounts of plasticizers, the mixed polymers may be utilized as a lacquer resin, or insulating material. Saponification of the polyvinyl ester can be followed without cessation of operation by condensation of the resulting polyvinyl alcohol with aldehyde, using hydrochloric acid as medium and ethyl alcohol as accelerator. The condensation products are employed for varnishes, motion picture films, records and artificial fibers.<sup>62</sup> Hard thermoplastic products are obtained from a mixture of vinyl and acrylic esters by saponification with aqueous sodium hydroxide and treatment with sulphuric acid. The resultant product may be used for making films, filaments and coating compositions.<sup>63</sup>

Yacca gum with vinyl ester polymers and vinyl ester-aldehyde products yields a material possessing lower water-absorbing and higher warp-resisting qualities.<sup>64</sup>

Vinyl resins are used in making composite articles with metals. The metal is corroded before applying the resin and the coated object is heated and cooled under pressure.<sup>65</sup>

Polyvinyl alcohol, as previously noted, may be treated with an alkylene oxide at ordinary or raised temperature and pressure, to yield water-soluble products used as thickeners, sizes or plastic masses.<sup>66</sup> An accelerator such as a tertiary organic base may be employed. Vinyl acetate forms one constituent of an adhesive for uniting celluloid to glass (either vinyl acetate, glyceryl phthalate and a plasticizer or vinyl acetate, formaldehyde-toluene sulphonamide and dibutyl phthalate).<sup>67</sup> A splinterless glass<sup>68</sup> can be made by interposing between sheets of glass a highly viscous and elastic layer of polyvinyl alcohol. The polymerized ester, either alone or condensed with aldehydes, is also used in manufacturing laminated glass.<sup>69</sup> When vinyl ester resins undergo partial acetal transformation, they become more soluble in the usual solvents and can be utilized for making films, adhesives and molding compositions. The flexibility and water-resistance of the films are increased when a non-drying oil is added.<sup>70</sup>

Polyvinyl alcohols react with  $\alpha$ -haloalkyl ethers in the presence of a hydrogen halide and a catalyst (zinc, iron or aluminum chloride) to form compositions for molding, insulating materials, adhesives and manufacture of films and threads.<sup>71</sup>

<sup>60</sup> D. T. Jones, R. Burns and A. Renfrew, British P. 407,050, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 4926.

<sup>61</sup> F. Groff, British P. 388,309, 1932, to Carbide & Carbon Chem. Corp.; *Brit. Chem. Abs. B*, 1933, 357. French P. 758,454, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3197.

<sup>62</sup> British P. 409,507, 1934, to Soc. Nobel française; *Chem. Abs.*, 1934, 28, 6357.

<sup>63</sup> H. Fikentscher, German P. 601,324, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 7443. British P. 416,885, 1933; *Chem. Abs.*, 1934, 28, 1022.

<sup>64</sup> British P. 414,703, 1933, to Shawinigan Chemicals, Ltd.; *Brit. Chem. Abs. B*, 1934, 933.

<sup>65</sup> French P. 738,886, 1932, to Carbide & Carbon Chem. Corp.; *Chem. Abs.*, 1933, 27, 2052.

<sup>66</sup> A. Schmidt, G. Balle and K. Eisfeld, German P. 575,141, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3453.

<sup>67</sup> H. Ford and R. H. McCarroll, British P. 365,823, 1930, to Ford Motor Co.; *Chem. Abs.*, 1933, 27, 2260.

<sup>68</sup> British P. 363,567, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3576. British P. 367,633, 1930; *Chem. Abs.*, 1933, 27, 3053.

<sup>69</sup> French P. 674,890, 1929, to Pollopos Ltd.; *Chem. Abs.*, 1930, 24, 2852.

<sup>70</sup> British P. 416,412 and 416,413, 1934, to Shawinigan Chemicals, Ltd.; *Chem. Abs.*, 1935, 29, 1176, 1177.

<sup>71</sup> British P. 414,699, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 834.

On adding monochlorodimethyl ether drop by drop to a boiling chloroform suspension of polyvinyl alcohol, a white solid is precipitated.<sup>99</sup>

Another process for the manufacture of artificial threads has been advanced,<sup>99</sup> in which a polymerized vinyl compound dissolved in cyclohexanone is utilized together with a softening agent. This is spun into a precipitating-bath containing acetic acid, sodium perchlorate or sodium thiocyanate, and the swollen threads are stretched in several increasing steps and then shrunk, before collecting on the receiving device.

Among other applications, polyvinyl alcohol has found use in food preparations. Haehnel and Herrmann<sup>100</sup> have proposed the utilization of polyvinyl alcohol and its derivatives as gelatinizing agents in the manufacture of fruit jellies. The addition of about 1 per cent of polymerized vinyl alcohol to ice cream preparations before freezing is said to improve the texture of the product by eliminating the formation of ice crystals.<sup>101</sup>

To prepare carboxylic acids from aldehyde<sup>102</sup> or polyvinyl condensation products, the resins are heated with an excess of sodium hydroxide at a temperature sufficient to split off the maximum amount of hydrogen, extracted with water and the product precipitated with hydrochloric acid.<sup>103</sup>

<sup>99</sup> French P. 765,832, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6956.

<sup>99</sup> British P. 387,976, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 301.

<sup>100</sup> W. Haehnel and W. O. Herrmann, German P. 589,201, 1933, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 1423.

<sup>101</sup> W. O. Herrmann and W. Haehnel, U. S. P. 1,921,124, Aug. 8, 1933, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 5122.

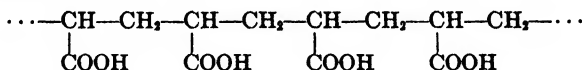
<sup>102</sup> See Chapter 23.

<sup>103</sup> W. Haehnel and W. O. Herrmann, German P. 588,762, 1933, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 2018.

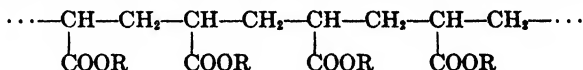
## Chapter 53

### Polyacrylic Acid and Its Derivatives

Acrylic acid,  $\text{CH}_2=\text{CHCOOH}$ , is a colorless liquid which boils at  $141^\circ\text{C}$ . and has an odor like that of acetic acid. Structurally, this acid (as well as its derivatives such as the esters, nitrile, amide and acid chloride) has many points in common with vinyl alcohol and the esters described in the preceding chapters.<sup>1</sup> Acrylic acid is ethylene with one hydrogen atom replaced by the negative carboxyl group,  $-\text{COOH}$ . Like the vinyl esters, it polymerizes to a solid, which is believed to have the structure:



Polyacrylic acid would thus be classed as a polybasic acid. The esters of acrylic acid also undergo a change to yield solids that seem to have the structure:



Chemical differences between the hydrolytic products of polyvinyl esters and polyacrylic derivatives form the basis for describing them separately. Polyvinyl esters give polyvinyl alcohol as one of the products of hydrolysis. Polyacrylic acid derivatives<sup>2</sup> yield polyacrylic acid. Although ordinary polybasic acids are crystalline, polyacrylic acid is amorphous, as shown by x-ray examination.<sup>3</sup> Staudinger considers that the properties of polyvinyl alcohol are such as to class it with starch, but the properties of polyacrylic acid (especially its alkali salts) warrant its being considered an analogue of proteins.<sup>4</sup>

#### PREPARATION OF ACRYLIC ACID

General methods by which acrylic acid and related acids are obtained include: oxidation of the corresponding aldehyde or alcohol, dehydration of  $\beta$ -hydroxypropionic acid, and elimination of hydrogen halide or halogen from halogenated propionic acids.

Oxidation of acrolein by means of air or by shaking it with silver oxide was one of the early methods suggested.<sup>5</sup> The oxidation of this aldehyde in an organic solvent with air or oxygen is likewise feasible. For example, a 50 per cent solution of acrolein in benzene kept for 14 hours at  $50^\circ\text{C}$ . under oxygen at a pressure of 10 atmospheres gives a 73 per cent yield of the acid. When the reaction is stopped before more than about 80 per cent of the aldehyde has been oxidized,

<sup>1</sup> See Chapters 51 and 52. Compare also styrene (Chapter 11), another negatively substituted ethylene.

<sup>2</sup> According to H. Staudinger and E. Trommsdorff (*Ann.*, 1933, 502, 212; *Chem. Abs.*, 1933, 27, 4313), ethyl polyacrylate is more difficult to hydrolyse than is polyvinyl acetate.

<sup>3</sup> H. Staudinger and E. Urech, *Helv. Chim. Acta*, 1930, 12, 111; *Brit. Chem. Abs. A*, 1930, 64.

<sup>4</sup> Likewise, H. Staudinger considers that polystyrene (see Chapter 11) is structurally a molecular model for rubber and that polyethylene oxide (see Chapter 50) is a model for carbohydrates.

<sup>5</sup> Redtenbacher, *Ann.*, 1834, 47, 128.

polymerization of the acid is avoided.\* Oxidation of allyl alcohol yields acrylic acid along with other substances.<sup>7</sup>

When salts of hydracrylic acid<sup>8</sup> ( $\beta$ -hydroxypropionic acid) are heated (or when the acid itself<sup>9</sup> is distilled) dehydration to the unsaturated acid results. Van der Burg<sup>10</sup> formed acrylic acid by treating sodium hydracrylate (prepared by hydrolyzing ethylene cyanohydrin by means of a solution of caustic soda) with concentrated sulphuric acid.  $\beta$ -Chloropropionic acid decomposes when heated alone,<sup>11</sup> or with aqueous alkalis,<sup>12</sup> to give acrylic acid. Hydrochloric acid is also removed from  $\beta$ -chloropropionic acid or its esters by passing the vaporized acid or ester over a catalyst, e.g., active carbon, at 180-270°C.<sup>13</sup> Under similar conditions  $\alpha$ -bromopropionic acid yields some lactic acid as well.<sup>14</sup> Acrylic acid is obtained when  $\beta$ -iodopropionic acid is heated with alcoholic potash,<sup>15</sup> lead oxide<sup>16</sup> or sodium carbonate,<sup>17</sup> or when  $\alpha,\beta$ -dibromopropionic acid is treated with zinc<sup>18</sup> or other metals,<sup>19</sup> or when heated with aqueous potassium iodide solution.<sup>20</sup> In a similar manner, using high temperatures, acrylic acid may be produced from  $\alpha,\beta$ -dichloropropionic acid.<sup>21</sup>  $\alpha$ -Bromopropionaldehyde dimethyl acetal when shaken with lead hydroxide or moist silver oxide is another source of the acid.<sup>22</sup>

A proposed synthesis of acrylic acid from ethylene and carbon dioxide involves bringing the two gases into reaction at 200-300°C. in the presence of a catalyst. The latter may be an acid gas, a salt or an oxide, for example sulphur dioxide or sodium acid phosphate. Also a mixture of ethyl alcohol and carbon dioxide can be passed first over a dehydration catalyst to give ethylene and then over the catalyst for the formation of acrylic acid. The acid can be polymerized to a resin without its intermediate isolation.<sup>23</sup>

Hydrolysis of the nitrile of acrylic acid (vinyl cyanide) also gives acrylic acid. Baum and Herrmann<sup>24</sup> recovered vinyl cyanide after passing a mixture of acetylene and hydrogen cyanide over heated barium cyanide or activated charcoal.

### POLYMERIZATION OF ACRYLIC ACID

On standing, acrylic acid polymerizes<sup>25</sup> under the influence of light or heat and in the presence of a catalyst. As with vinyl acetate, the polymerization of both the acid and its esters by ultraviolet light is much slower in air or oxygen than in nitrogen or carbon dioxide. Staudinger and Kohlschütter<sup>26</sup> observed that

\* W. Bauer and P. Weisert, U. S. P. 1,911,219, May 30, 1933, to Röhm & Haas A.-G.; *Chem. Abs.*, 1933, 27, 3949. British P. 373,326, 1931; *Brit. Chem. Abs. B*, 1932, 832. French P. 713,261, 1931; *Chem. Abs.*, 1932, 26, 1622.

<sup>7</sup> A mixture of air and allyl alcohol passed over hot platinum yields only a small amount of acrylic acid. J. A. Trillat, *Bull. soc. chim.*, 1903, (3) 29, 41; *J.C.S.*, 1903, 84 (1), 222. For electrolytic oxidation of allyl alcohol, see H. D. Law, *J. C. S.*, 1906, 89, 1449.

<sup>8</sup> F. Beilstein, *Ann.*, 1862, 122, 372. J. Wislicenus, *Ann.*, 1873, 166, 14; 1874, 174, 286; *J.C.S.*, 1873, 26, 490; 1875, 28, 355.

<sup>9</sup> Moldenhauer, *Ann.*, 1864, 131, 335. J. Wislicenus, *ibid.*, 1873, 166, 23; *J.C.S.*, 1873, 26, 490.

<sup>10</sup> J. H. N. Van der Burg, *Rec. trav. chim.*, 1922, 41, 21; *Chem. Abs.*, 1922, 16, 1210.

<sup>11</sup> Krestownikov, *J. Russ. Phys.-Chem. Soc.*, 1879, 11, 250.

<sup>12</sup> C. Moureu, *Ann. chim.*, 1894, (7) 2, 172; C. Moureu, M. Murat and L. Tampier, *Compt. rend.*, 1921, 172, 1267; *Chem. Abs.*, 1922, 16, 55. See also C. N. Rüber and J. Schetelig, *Z. physik. chem.*, 1904, 48, 348; *J.C.S.*, 1904, 86 (3), 539.

<sup>13</sup> W. Bauer and H. Lauth, German P. 607,483, 1934, to Röhm & Haas A.-G.; *Chem. Abs.*, 1935, 29, 1635.

<sup>14</sup> W. Loosen and E. Kowski, *Ann.*, 1905, 342, 128; *J.C.S.*, 1906, 90 (1), 59.

<sup>15</sup> W. von Schneider and E. Erlensmeyer, *Ber.*, 1870, 3, 340.

<sup>16</sup> Beilstein, *Ann.*, 1862, 122, 372. J. Wislicenus, *ibid.*, 1873, 166, 2; *J.C.S.*, 1873, 26, 403.

<sup>17</sup> A. Wöhler, *J. prakt. Chem.*, 1900, (2) 61, 211; *J.C.S.*, 1900, 78 (1), 425.

<sup>18</sup> W. Caspary and B. Tollens, *Ann.*, 1873, 167, 241; *Chem. Zentr.*, 1873, 581.

<sup>19</sup> E. Billmann, *J. prakt. Chem.*, 1900, (2) 61, 322; *J.C.S.*, 1900, 78 (1), 425.

<sup>20</sup> V. von Zotta, *Ann.*, 1873, 192, 162; *J.C.S.*, 1873, 34, 782.

<sup>21</sup> German P. 575,423, 1923, addn. to 555,933, to Röhm & Haas A.-G.; *Chem. Abs.*, 1923, 27, 5756.

<sup>22</sup> A. Wohl, *Ber.*, 1908, 41, 3605; *Chem. Abs.*, 1909, 3, 185.

<sup>23</sup> German P. 553,179, 1929, to Röhm & Haas A.-G.; *Chem. Abs.*, 1932, 26, 4610.

<sup>24</sup> E. Baum and W. O. Herrmann, German P. 559,734, 1930, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 735.

<sup>25</sup> H. Lössmann, *Ann.*, 1872, 163, 369; *J.C.S.*, 1872, 25, 1002. C. Moureu, M. Murat and L. Tampier, *Ann. chim.*, 1921, 15, 261; *Chem. Abs.*, 1922, 16, 55.

<sup>26</sup> H. Staudinger and H. W. Kohlschütter, *Ber.*, 1931, 64, 2091; *Chem. Abs.*, 1932, 26, 1243.

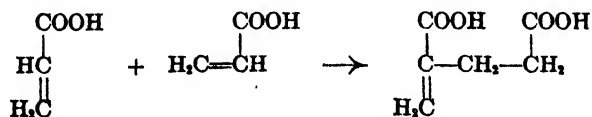
acrylic acid, illuminated in the presence of air or oxygen, underwent an especially rapid polymerization when, without discontinuing the illumination, the oxygen was displaced by carbon dioxide. Oxygen inhibits the photopolymerization not only of pure acrylic acid but also of its aqueous solutions. On the other hand, it accelerates the thermal polymerization. Addition of a small amount of hydroquinone prevents polymerization. Pure acrylic acid can be kept unchanged at ordinary temperature for a long time. On applying heat, partial polymer-formation takes place below 100°C. The temperature to which this acrylic acid polymerization product has been raised determines the readiness with which it can polymerize still further. Above 100°C. polymerization occurs rapidly and the heat of the reaction is such as to produce very high pressures when sealed tubes are used. The products obtained by polymerization of different preparations of acrylic acid vary in appearance, some being glassy and others, porcelain-like.

Polyacrylic acid is insoluble in the monomeric acid and separates as a solid phase during polymerization, instead of forming an increasingly viscous solution as in the case of vinyl acetate and styrene. In this respect it resembles polyvinyl halides. On the other hand, the polyacrylic esters are soluble in the monomers.

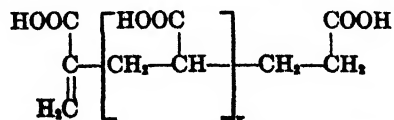
Catalysts like Florida earth have no influence on acrylic acid. Also, according to Staudinger and Urech,<sup>17</sup> stannic chloride, which is very effective with indene and styrene, does not polymerize acrylic acid. On adding it to the acid a violent reaction occurs but on decomposition of the complex which is formed, by means of water or alcohol, only the monomeric acid can be recovered. The stannic chloride compound is probably too stable to build up into large molecules.

The mechanism of the polymerization of acrylic acid is believed by Staudinger and Kohlschütter<sup>18</sup> to involve the activation of certain molecules through the agency of light or catalysts, and subsequent addition of other molecules to the activated molecules to form long chains. This addition of molecules continues until the energy of the original activated molecule has been dissipated. The growing chains initially have free end-valences but these eventually become stabilized by ring-formation or by other means of saturation such as combination with catalysts, solvent molecules or impurities that may be present.

That a chain reaction of many steps is the probable course is made plausible by the fact that monomeric acid can be distilled away from the polymerized material but there is no indication of low polymers such as the dimer or trimer. Low polymers of the latter class have been prepared from acrylic esters by means of condensing agents such as sodium methylate, but their mechanism of formation is to be ascribed to an entirely different process, namely, migration of a hydrogen atom from one molecule to saturate a double bond of a second molecule of ester. The means of polymerization which leads to unsaturated, low-molecular compounds is illustrated by the following equation:



This type of reaction may lead to slightly higher polymers having the structure:



<sup>17</sup> H. Staudinger and E. Urech, *Helv. Chim. Acta*, 1929, 12, 113; *Brit. Chem. Abs. A*, 1929, 64.

<sup>18</sup> H. Staudinger and H. W. Kohlschütter, *loc. cit.*

but it does not yield saturated polymers of high molecular weight. The formation of unsaturated low-molecular products in this way involves splitting one molecule and adding the H— and carboxy-vinyl residue to saturate another molecule, and so on. The products thus formed are so manifestly different from the saturated high-molecular polyacrylic acid of photo- or thermopolymerization that the conception of different mechanisms for their formation seems entirely justified.

Being completely saturated, polyacrylic acid shows no bromine absorption. It is also stable towards potassium permanganate and concentrated nitric acid. In contrast with polystyrene,<sup>20</sup> when heated above 300°C. it does not yield the monomer. Instead, pyrolytic products of the latter are obtained and in this respect it resembles the polyvinyl esters.

As with other polymeric products, a single molecular species is not formed by polymerization of acrylic acid or its derivatives, but a mixture consisting of molecules ranging in size from at least 100 monomeric units upwards, the average molecular size depending upon the conditions employed in the polymerization. Polyacrylic acid dissolves colloiddally in water and also in formamide. It is difficultly soluble in alcohol and insoluble in typical organic solvents like benzene, chloroform, acetone and acetic acid. The readiness with which it dissolves in water is dependent upon the way in which it is prepared. Only polymers prepared at a temperature above 120°C. dissolve easily. Those obtained at lower temperatures either yield exceedingly viscous solutions, or merely swell. Prepared at elevated temperatures, polyacrylic acid has a lower molecular weight than when prepared at low temperatures.

An aqueous solution of polyacrylic acid can be made by dissolving the water-soluble polymers. Also, since it is soluble in water, acrylic acid can be polymerized in this solvent to form a solution of the polymer. Hydrolysis of polyacrylonitrile in the presence of water also gives an aqueous solution of the polymerized acid. Neutralization of aqueous solutions of polyacrylic acid by means of alkalis forms soluble salts of the acid and greatly increases the viscosity. Sodium polyacrylate has been suggested as a dispersing and emulsifying agent for pastes of water-insoluble dyestuffs.<sup>21</sup> Color-lakes formed from acid dyes in the presence of an aqueous solution of sodium polyacrylate or other water-soluble products of high molecular weight, such as alkali salts of the co-polymers of acrylic acid and styrene, vinyl esters or vinyl ethers, have less covering power than ordinary lakes but are non-bronzing.<sup>22</sup> Acrylic acid has been mentioned as a constituent of a mixture which yields a synthetic rubber after polymerization and vulcanization.<sup>23</sup> Varnish constituents, germicides and dye compounds are formed by reacting polyacrylic acid with organic bases or their salts (e.g., quinine sulphate, nicotine, methylene blue). The co-polymers of styrene and maleic anhydride can be substituted for polyacrylic acid to obtain the same type of products.<sup>24</sup>

#### ESTERS OF ACRYLIC ACID

Kahlbaum<sup>25</sup> found that methyl acrylate, on long standing in the sunlight or when warmed, changed into a transparent, odorless mass of density 1.222, which decomposed when melted. It was insoluble in acids, alkalis, water, alcohol and ether, but swelled slightly in boiling acetic acid or benzene. When heated under reduced pressure a soluble liquid polymeric modification distilled (b.p. 190°C. at

<sup>20</sup> See Chapter 11.

<sup>21</sup> British P. 269,915, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 764.

<sup>22</sup> British P. 359,949, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 322. French P. 717,604, 1931; *Chem. Abs.*, 1933, 26, 2875.

<sup>23</sup> French P. 42,335, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5577.

<sup>24</sup> French P. 703,943, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5190.

<sup>25</sup> G. W. A. Kahlbaum, *Ber.*, 1890, 13, 2343; 1895, 18, 2103.



100 mm.) which had an aromatic odor. Weger<sup>50</sup> noticed that when the methyl, ethyl or propyl esters of acrylic acid were distilled, they were partially converted into solids. Allyl acrylate polymerizes quite rapidly when exposed to sunlight.<sup>51</sup>

Although polyacrylic acid separates as a crust-like mass when the acid is allowed to polymerize in the light,<sup>52</sup> acrylic esters under the same conditions gradually increase in viscosity and pass from a viscous liquid to a glassy or rubber-like solid. Polyacrylic esters are soluble in the monomeric esters and in this respect are comparable with vinyl acetate and styrene. Polyacrylic esters also differ from the polymerized acid in solubility. They are insoluble in water and alcohol but dissolve in benzene, acetone and chloroform. The readiness with which they dissolve depends upon the extent to which the esters are polymerized. Only those polymerized at temperatures above about 120°C. dissolve freely; those obtained by polymerization at lower temperatures either merely swell or yield solutions of very high viscosity. However, if the temperature is increased sufficiently, not only will initially insoluble polymers gradually dissolve but also the viscosity of the more viscous solutions will be reduced. This is caused by the instability of the highest polymers at elevated temperatures and their tendency to break down into smaller, more soluble products.<sup>53</sup>

Staudinger and Trommsdorff<sup>54</sup> prepared a series of polymers of ethyl acrylate corresponding in degree of polymerization to from about 20 for the lowest polymers to more than 1700 for the highest. The lower polymers were obtained by dissolving ethyl acrylate in butyl acetate and heating the solution for varying periods. The highest was obtained from the pure ester by heating it at 100°C. for 12 days. Table 56 shows the molecular weight and the degree of polymerization; also the change in the properties of the different members of the series as the degree of polymerization increases:

TABLE 56.—Polymeric Modifications of Ethyl Acrylate.

No.	Molecular Weight	Degree of Polymerization	Properties of Polymers
1.	2200	22	A viscous, colorless oil. Dissolves easily in benzene. Solution of low viscosity.
2.	4000	40	Somewhat more viscous than 1.
3.	7800	78	Tough, somewhat fluid mass. Adheres to glass. Can be drawn out into threads.
4.	14500	145	Tougher than 3. Strong adhesion to glass. Can be drawn out into threads. Swells slightly in benzene, then dissolves.
5.	22500	225	Tougher than 4. Swells somewhat in benzene, then dissolves.
6.	41000	410	Very tough. Non-flowable. Difficultly drawn out into threads. Swells in benzene, then dissolves.
7.	175000	1750	Tough, elastic, rubber-like mass. Swells greatly in benzene, then dissolves giving solution of high viscosity.
8.	Too high to determine.		Very tough, elastic, rubber-like mass. Insoluble in benzene, but swells to 50 times its initial volume.

#### PREPARATION OF ACRYLIC ESTERS

Esters of acrylic acid are formed by esterification of acrylic acid or its functional derivatives. Also they can be formed in many of the same ways in which acrylic

<sup>50</sup> F. Weger, *Ann.*, 1888, 221, 86; *J.C.S.*, 1884, 46, 8.

<sup>51</sup> W. Caspary and B. Tollens, *Ann.*, 1873, 167, 241; *Chem. Zentr.*, 1873, 531.

<sup>52</sup> This is analogous to the polymerization of vinyl chloride under the influence of light. See Chapter 51. Compare also cuprene, Chapter 8.

<sup>53</sup> H. Staudinger and E. Urech, *Helv. Chim. Acta*, 1929, 12, 1128; *Brit. Chem. Abs. A*, 1930, 64.

<sup>54</sup> H. Staudinger and E. Trommsdorff, *Ann.*, 1933, 502, 207; *Chem. Abs.*, 1933, 27, 4213.

acid is produced, substituting an ester for the acid used in those reactions. The ethyl ester can be made by dissolving ethyl  $\alpha,\beta$ -dibromopropionate in alcohol and treating the solution with zinc and sulphuric acid<sup>40</sup> or with zinc alone.<sup>41</sup> The methyl ester of  $\alpha,\beta$ -dichloropropionic acid, dissolved in methyl alcohol and heated with zinc which has been activated by the addition of a small amount of mercury or a halogen, yields methyl acrylate.<sup>42</sup> Also,  $\beta$ -chloropropionic esters yield esters of acrylic acid when treated with alcoholic potash,<sup>43</sup> or when heated with a contact mass prepared by first impregnating active carbon with water glass, drying, and subsequently mixing with phosphoric acid and heating to 200°C.<sup>44</sup> An alternative method consists in distilling the  $\beta$ -chloropropionic ester with concentrated sulphuric acid to give a yield of 85-90 per cent of the desired ester.<sup>45</sup> Acrylic esters may also be synthesized by heating gradually to 160°C.,  $\beta$ -hydroxypropionitrile in an acid medium along with the appropriate alcohol and a dehydrating agent.<sup>46</sup> Ethylene cyanohydrin<sup>47</sup> (hydracrylonitrile) treated in alcoholic solution with concentrated sulphuric acid, and ethyl hydracrylate<sup>48</sup> heated at about 200°C. with phosphoric acid or with silica gel impregnated with sulphuric acid, are dehydrated to form acrylic esters.<sup>49</sup> Good yields of acrylic esters have been obtained by heating alcoholic solutions of the acid chloride with an acid-binding reagent.<sup>50</sup>

#### OTHER FUNCTIONAL DERIVATIVES OF ACRYLIC ACID

Acrylic acid nitrile,<sup>51</sup> chloride,<sup>52</sup> amide<sup>53</sup> and anilide<sup>54</sup> also polymerize. According to Staudinger and Urech,<sup>55</sup> the polymerized amide is an insoluble horn-like mass. In the polymerization of the amide by heat, ammonia is given off and an imide is partially formed. Ammonia can split out between adjacent  $\text{NH}_2$ -groups in the chain or between  $\text{NH}_2$ -groups in separate chains and leads to a linking of the chains and formation of an insoluble, 3-dimensional macromolecule instead of a linear molecule:

<sup>40</sup> W. Caspary and B. Tollens, *Ann.*, 1873, 167, 248; *Chem. Zentr.*, 1873, 531.

<sup>41</sup> A. Michael and O. Schulthess, *J. prakt. Chem.*, 1891, (2) 43, 589; *J.C.S.*, 1891, 60, 1184. See also O. Röhm, *Ber.*, 1900, 34, 573.

<sup>42</sup> German P. 555,933, 1929, to Röhm & Haas A.-G.; *Chem. Abs.*, 1932, 26, 5964.

<sup>43</sup> W. Bauer, U. S. P. 1,864,884, June 28, 1932, to Röhm & Haas A.-G.; *Chem. Abs.*, 1932, 26, 4345. British P. 316,547, 1929; *Chem. Abs.*, 1930, 24, 1867. French P. 678,744, 1929; *Chem. Abs.*, 1930, 24, 3516. German P. 546,141, 1928; *Chem. Abs.*, 1932, 26, 3261.

<sup>44</sup> British P. 351,518, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2988. French P. 709,627, 1931; *Chem. Abs.*, 1932, 26, 994.

<sup>45</sup> B. Jacobi and H. Fikentscher, U. S. P. 1,934,613, Nov. 7, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 483. German P. 571,524, 1933; *Chem. Abs.*, 1933, 27, 4243.

<sup>46</sup> W. Bauer, German P. 571,123, 1928, to Röhm & Haas A.-G.; *Chem. Abs.*, 1933, 27, 2692.

<sup>47</sup> W. Bauer, U. S. P. 1,829,208, Oct. 27, 1931, to Röhm & Haas A.-G.; *Chem. Abs.*, 1932, 26, 735. British P. 313,877, 1929; *Chem. Abs.*, 1930, 24, 1120.

<sup>48</sup> W. Bauer, U. S. P. 1,890,277, Dec. 6, 1932, to Röhm & Haas A.-G.; *Chem. Abs.*, 1933, 27, 1639. British P. 341,153, 1930; *Brit. Chem. Abs. B.*, 1932, 251. French P. 707,154, 1930; *Chem. Abs.*, 1932, 26, 479. French P. 675,327, 1929; *Chem. Abs.*, 1930, 24, 2756. German P. 575,724, 1933; *Chem. Abs.*, 1933, 27, 4244.

<sup>49</sup> According to K. N. Welch (*J.C.S.*, 1930, 257) ethyl di(hydroxymethyl)malonate decomposes when heated, giving large quantities of tar.

<sup>50</sup> W. Bauer and H. Lauth, U. S. P. 1,951,782, Mar. 20, 1934, to Röhm & Haas A.-G.; *Chem. Abs.*, 1934, 28, 3417. German P. 570,955, 1933; *Chem. Abs.*, 1933, 27, 4244.

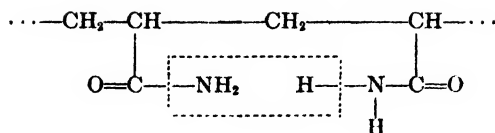
<sup>51</sup> J. H. N. Van der Burg, *Rec. trav. chim.*, 1922, 41, 21; *Chem. Abs.*, 1922, 16, 1210. Cyanooctyl chloride changes after a few days to a brown resin. See G. Schroeter, C. Seidler, M. Sulzbacher and R. Kanits, *Ber.*, 1932, 65, 432; *Chem. Abs.*, 1932, 26, 2982.

<sup>52</sup> C. Moureu (*Bull. soc. chim.*, 1893, (3) 9, 390; *J.C.S.*, 1893, 64 (1), 548) prepared the acid chloride by the reaction of sodium acrylate and phosphorus oxychloride. The acid chloride reacts with alcohols to form esters of  $\beta$ -chloropropionic acid. Another method of making the acid chloride consists in heating chloropropionyl chloride in contact with substances which extract hydrogen halide, such as barium chloride or alumina. See H. Fikentscher, German P. 577,040, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3960. British P. 338,079, 1930; *Chem. Abs.*, 1931, 25, 524. French P. 697,311, 1930; *Chem. Abs.*, 1931, 25, 3014.

<sup>53</sup> C. Moureu, *Ann. chim.*, 1894 (7) 2, 175.

<sup>54</sup> H. Staudinger and E. Urech, *Helv. Chim. Acta*, 1929, 12, 1182; *Brit. Chem. Abs. A*, 1930, 64.

<sup>55</sup> H. Staudinger and E. Urech, *loc. cit.*



The anilide, when heated for 3 days at 130°C., changes to a dark brown, horn-like product which is insoluble in water and in all organic solvents. A similar material results from heating polyacrylic acid chloride with aniline. The nitrile can be polymerized by emulsifying it with water and heating it to 100°C. with the addition of hydrogen peroxide. Polymerized acrylonitrile may be saponified to give polymeric acids from which the corresponding polyacrylic esters are derived.<sup>66</sup> Resinous products were obtained when Auwers and Ungemach<sup>67</sup> attempted to condense the nitrile with diazomethane. By heating acrylic acid chloride to 150°C. it polymerizes to a brown insoluble mass. Bases such as triethylene-tetramine or biperidyl serve as catalysts. Under the influence of ultraviolet light at ordinary temperatures an almost colorless, glassy product is obtained, which also is insoluble in all solvents. When polyacrylic acid is treated with phosphorus trichloride or thionyl chloride, the same type of insoluble product is obtained.

Soluble resins that were suggested for use with nitrocellulose in lacquers are obtained by treating the polymers of acrylic acid chloride or nitrile under pressure at 35-150°C. with substances capable of reacting with the Cl- or CN group. Water reacts to form polyacrylic acid, or with less than an equivalent amount of water present to form polyacrylic anhydride. Aqueous solutions of alkalies give salts of polyacrylic acid. Ammonia, primary and secondary amines form the polyamide and substituted polyamides. Other reactants which can be used are alcohols, hydrogen sulphide, mercaptans, or malonic and acetoacetic esters. Also co-polymers of acrylic acid chloride or nitrile with vinyl acetate, acrylic esters or styrene can be treated in the same way.<sup>68</sup> A solution of sodium polyacrylate, obtained by hydrolysis of polymerized acrylonitrile by means of sodium hydroxide solution, is recommended as a dispersion agent for preparation of pastes of water-insoluble dyestuffs for printing or as an emulsifying agent for oil-water emulsions.<sup>69</sup>

#### POLYMERIZATION OF ACRYLIC ACID DERIVATIVES

Acrylic acid and its derivatives can be polymerized by heating them in the presence of oxygen or organic peroxides. A solvent such as acetone may be present.<sup>60</sup> Also mixtures of acrylic acid derivatives with other polymerizable substances can be subjected to light or heat in the presence of a polymerization catalyst to yield co-polymers. For example, a mixture of ethyl acrylate with vinyl acetate may be polymerized,<sup>61</sup> or a mixture of acrylic acid, its esters or nitrile with styrene.<sup>62</sup> The co-polymerization of acrylic and vinyl esters results in the formation of products hydrolyzable to lactones when treated with strong acids.<sup>63</sup> In general,

<sup>60</sup> H. Mark and H. Fikentscher, German P. 580,351, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4816.

<sup>61</sup> K. von Auwers and O. Ungemach, *Ber.*, 1933, 66, 1196.

<sup>62</sup> H. Mark and H. Fikentscher, U. S. P. 1,984,417, Dec. 18, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 856. British P. 351,508, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3138. French P. 697,437, 1930; *Chem. Abs.*, 1931, 25, 3018.

<sup>63</sup> British P. 369,915, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 764.

<sup>64</sup> British P. 304,681, 1928, to Röhm & Haas A.-G.; *Chem. Abs.*, 1929, 23, 4784. French P. 663,711, 1928; *Chem. Abs.*, 1930, 24, 639.

<sup>65</sup> French P. 697,693, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 3136.

<sup>66</sup> British P. 371,896, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 688. See also French P. 715,961, 1931; *Chem. Abs.*, 1932, 26, 2653.

<sup>67</sup> French P. 765,272, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6956. British P. 416,885, 1934; *Chem. Abs.*, 1935, 29, 1181.

co-polymers are insoluble in water and are recommended for forming threads, coatings or binding agents. Furthermore, acrylic acid derivatives can be polymerized in mixture with butadiene. Thus, a mixture of butadiene and acrylonitrile<sup>66a</sup> or acrylic esters<sup>66</sup> is heated and the co-polymers, after being milled with lamp-black, can be vulcanized to form rubber-like masses. Molded objects resembling celluloid are obtained by working, in the manner used for manufacture of celluloid, the co-polymers formed with vinyl chloride, acrylonitrile, acrylic acid, styrene or  $\beta$ -chlorobutadiene in mixture with acrylic esters, vinyl ethers or alkyl vinyl ketones.<sup>67</sup> A proportion of at least 20 per cent acrylic acid nitrile in the co-polymerization product mixture is stated to be advantageous.<sup>68</sup> The polymerization of these compounds may be carried out in a paraffin oil solution, and since the polymers, so formed, are insoluble in this solvent the recovery of the resinous products is facilitated.<sup>67</sup> Acrylic acid derivatives can also be polymerized with maleic anhydride to form heteropolymers.<sup>69</sup>

Emulsions of acrylic esters containing a polymerization catalyst can be heated or exposed to light and the polymer afterwards separated. For example, methyl acrylate, emulsified with water containing sodium isopropyl-naphthalenesulphonate and hydrogen peroxide, and heated to 70-90°C., yields a latex which can be precipitated by addition of hydrochloric acid. This product can be formed into rubber-like threads or films. Other polymerizable substances such as styrene, acrylic acid, acrylonitrile, butyl methacrylate or vinyl acetate can be mixed with the acrylic ester before polymerization,<sup>70</sup> and the resulting aqueous dispersions may be used as adhesives.<sup>70</sup> Another polymerization process for methyl acrylate consists in emulsifying the ester in water with sulphonated castor oil as emulsifying agent and heating in a closed vessel with 1 per cent of a peroxide catalyst. As soon as the desired degree of polymerization is reached the reaction is terminated by addition of cold water. This makes the reaction controllable even in large-scale operations. Vinyl acetate may be mixed with the acrylic ester and a co-polymer of the two obtained in this way.<sup>71</sup> Co-polymers of acrylic acid derivatives and vinyl ethers are also formed by emulsifying the mixture and subjecting the emulsion to one of the above treatments. Vinyl ethyl or butyl ether, or glycol vinyl ethyl ether can be mixed with acrylonitrile or methyl acrylate to give products that range from rubber-like to celluloid-like masses.<sup>72</sup>

Dykstra<sup>73</sup> polymerized esters of other unsaturated acids (maleic or fumaric acids and their homologues) with the aid of heat and actinic light. Catalysts such as benzoyl peroxide and triethyl-lead acetate may be used to advantage in this reaction, and the resins, so obtained, are said to be useful in the preparation of lacquers.

<sup>66a</sup> British P. 360,821, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1236. French P. 715,962, 1931; *Chem. Abs.*, 1933, 26, 3085.

<sup>66</sup> British P. 360,823, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1236. French P. 715,963, 1931; *Chem. Abs.*, 1933, 26, 3085.

<sup>67</sup> French P. 723,861, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 6081.

<sup>68</sup> British P. 411,960, 1934, to Röhm & Haas A.-G.; *Chem. Abs.*, 1934, 28, 6956.

<sup>69</sup> British P. 404,604, 1933, to Röhm & Haas A.-G.; *Brit. Chem. Abs. B*, 1934, 244. French P. 753,045, 1933; *Chem. Abs.*, 1934, 28, 783.

<sup>70</sup> A. Voss and E. Diekhäuser, German P. 540,101, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1813. British P. 376,479, 1931; *Brit. Chem. Abs. B*, 1932, 948. French P. 719,145, 1931; *Chem. Abs.*, 1932, 26, 3392.

<sup>71</sup> British P. 338,584, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 172. French P. 710,901, 1931; *Chem. Abs.*, 1933, 26, 1830.

<sup>72</sup> French P. 773,841, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2363.

<sup>73</sup> British P. 374,436, 1931, to Röhm & Haas A.-G.; *Brit. Chem. Abs. B*, 1933, 378. French P. 709,991, 1931; *Chem. Abs.*, 1933, 26, 994. For a review of the preparation of co-polymerized acrylic esters and vinyl acetate products see F. Ohl, *Nitrocellulose*, 1934, 5, 66; *Chem. Abs.*, 1934, 28, 4579.

<sup>74</sup> British P. 373,643, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 851.

<sup>75</sup> H. B. Dykstra, U. S. P. 1,945,507, Jan. 30, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 2367. British P. 389,467, 1933; *Chem. Abs.*, 1933, 27, 4790.

## USES OF POLYACRYLIC ACID DERIVATIVES

By evaporation of thin layers of solutions of polymerized acrylic esters, tough, clear films are formed which are water-resistant and durable. Röhm<sup>74</sup> proposed the use of such solutions as coating compositions, or for impregnating wood and fabrics. As solvents he used acetone or ethyl acetate. When exposed to ultra-violet light the films are hardened. Coating compositions can also be made by dissolving the unpolymerized esters in a solvent and carrying out the polymerization reaction in solution. Another coating composition consists of cellulose ethers mixed with polyacrylic esters, using an aqueous solution of water-soluble alkyl cellulose and an emulsion of the polymerized ester.<sup>75</sup>

A 10 per cent solution of ethyl polyacrylate in acetone is recommended as an adhesive for sticking paper or fabrics to metal.<sup>76</sup> As the cementing and supporting layer for laminated glass,<sup>77</sup> polyacrylic esters seem promising on account of their adhesion and rubbery nature, which lends non-splintering qualities to glass.<sup>78</sup> Giesel<sup>79</sup> has suggested the employment of ethyl or methyl polyacrylate for this purpose.<sup>80</sup> Cellophane or cellulose acetate coated with a polyacrylic ester yields non-brittle, transparent, binding sheets for shatterproof glass.<sup>81</sup> Methods for making compound glass have been described<sup>82</sup> in which the adhesive agent is prepared by polymerizing mixtures of unsaturated compounds containing derivatives of acrylic acid. For example, an adhesive for this purpose can be produced by polymerizing a mixture of methyl acrylate, vinyl cyanide and isoprene. The condensation product formed by the reaction between maleic anhydride and castor oil or 1,3-butylene glycol can be mixed with polyacrylic esters and serve to increase the adhesion to glass and to make the polymers less brittle when cold.<sup>83</sup> Copolymers of vinyl esters and acrylic esters have also been proposed for the supporting layer between glass plates.<sup>84</sup> These ester polymers are likewise used for attaching metal, textile, glass or leather surfaces to one another.<sup>85</sup> Their elasticity, insolubility in oil and water and light-resistance enhance their utility in making shatter-

<sup>74</sup> O. Röhm, German P. 295,340, 1915; *J.S.C.I.*, 1917, 35, 296. For a review of chemical and physical properties of polymerized acrylic esters with respect to their use as lacquer raw materials see A. W. Van Heuvelkerth, *Circ., Nat. Paint, Varnish and Lacquer Assoc.*, 1924, 472, 364.

<sup>75</sup> British P. 308,284, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 289. French P. 35,929, 1928, addn. to 615,876. German P. 542,267, 1927.

<sup>76</sup> British P. 311,339, 1929, to Röhm & Haas A.-G.; *Chem. Abs.*, 1930, 24, 931. French P. 673,939, 1929; *Chem. Abs.*, 1930, 24, 2590. See also W. Bauer, U. S. P. 1,382,946, Dec. 4, 1934, to Charles Lennig & Co.; *Chem. Abs.*, 1935, 29, 628. German P. 575,327, 1933, to Röhm & Haas A.-G.; *Chem. Abs.*, 1933, 27, 3870.

<sup>77</sup> See *Chem. Age (London)*, 1932, 27, 472.

<sup>78</sup> H. Staudinger and E. Trommsdorff (*Ann.*, 1933, 502, 212; *Chem. Abs.*, 1933, 27, 4213) noted that ethyl acrylate, polymerised to a degree corresponding to between 100 and 500 monomeric groups per molecule, shows very remarkable adhesion to glass. The lower polymers and also the polymers of higher degree do not show adhesion to as great an extent.

<sup>79</sup> E. Giesel, British P. 293,871, 1928; *Chem. Abs.*, 1929, 23, 1731. French P. 669,964, 1929; *Chem. Abs.*, 1930, 24, 1951.

<sup>80</sup> The adhesive (polymerized vinyl, acrylic or itaconic esters) for glass and interposed sheets of celluloid can be introduced between the properly spaced layers through a fine tube and the sheets united under heat and pressure. See W. L. Munro, U. S. P. 1,980,970, Nov. 13, 1934; *Chem. Abs.*, 1935, 29, 569. British P. 334,153, 1932, to Consortium für elektrochem. Ind. G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 106.

<sup>81</sup> L. J. B. Forbes and W. B. Hill, British P. 406,644, 1934, to Triplex (Northern) Ltd.; *Chem. Abs.*, 1934, 28, 4258.

<sup>82</sup> L. Vivian, D. Scorrach and J. Wilson, British P. 389,115, 1933, to Triplex Safety Glass Co., Ltd.; *Chem. Abs.*, 1933, 27, 5920. British P. 389,151, 1933; *Chem. Abs.*, 1933, 27, 5920. J. Wilson, British P. 389,106, 1933; *Chem. Abs.*, 1933, 27, 5920. D. Scorrach and J. Wilson, British P. 419,357, 1934; *Brit. Chem. Abs. B*, 1935, 33.

<sup>83</sup> G. Kränlein, A. Voss, and E. Dickhäuser, German P. 547,324, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 26, 3633. British P. 367,658, 1931, addn. to 349,353; *Brit. Chem. Abs. B*, 1933, 433. French P. 40,116, 1931, addn. to 695,330; *Chem. Abs.*, 1933, 27, 834.

<sup>84</sup> British P. 346,567, 1931, addn. to 349,353, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 807.

<sup>85</sup> F. Ohl, *Gelatine, Leim, Klebstoffe*, 1924, 2, 147; *Chem. Abs.*, 1924, 28, 7457.

proof glass.<sup>86</sup> Mixed with such resins as toluenesulphonamide-formaldehyde, polyacrylic esters are stable towards light and are plastic at low temperatures.<sup>87</sup>

A sheet of polyacrylic ester can be used alone as a glass substitute.<sup>88</sup> However, plasticizers such as phthalic esters or monacetin may be added to increase the viscosity and to make the layer tougher.<sup>89</sup> The sheet can also be strengthened by supporting it on a metal screen. For example, wire gauze is dipped into a concentrated solution of the polymer, lifted out and allowed to drain.<sup>90</sup>

Röhm<sup>91</sup> proposed a rubber substitute, made by heating a polymerized acrylic ester with sulphur. As a material for floor coverings or as a leather substitute, derivatives of polyacrylic acid are mixed with fillers (cork dust, talc and carbon black) and softeners.<sup>92</sup> Films and other colloidal products of high degree of polymerization acquire undesirable electric charges which are said to be reduced by including, during the preparation, polymeric carboxylic acids or their salts. A proposed resin of this kind consists of a mixture of polyacrylic acid and polyvinyl chloride, films of which may be formed from dichloromethane solution.<sup>93</sup> Insulation for wires or cables consists of polymerized acrylic acid, its esters, acid chloride or nitrile, together with paper, mica and linexyn.<sup>94</sup> Sheets impermeable to gases and suitable for gas-masks are made by pressing together alternate layers of leather, cloth or paper, and a film about 0.5 mm. thick of ethyl polyacrylate or polyvinyl acetate.<sup>95</sup>

Derivatives of polyacrylic acid possess characteristics favorable to the production of molding compositions and other artificial masses. Plastic materials may be formed by treating a chloroform solution of acrylic acid esters with chlorine in the presence of sunlight.<sup>96</sup> This method is said to impart improved mechanical properties to the product as well as to increase the softening point and resistance to solvents. A white porous mass was obtained from a chloroform solution of polymerized methyl acrylate by treating with chlorine, removing the resultant hydrochloric acid and blowing in steam. The product may be mixed with linseed oil to give a plastic material.<sup>97</sup> A mixture of methyl acrylate and vinyl acetate polymerized by heat, electrical energy or light in the presence of the usual catalysts yields a resin which may be molded.<sup>98</sup> The metallic (e.g., silver, mercuric, ferric, nickel, cobalt) polyacrylates and polymethacrylates are said to possess useful thermoplastic and film-forming properties.<sup>99</sup> Masses to be employed in making sound records are produced by kneading an iron powder with polyacrylic compounds until the agglomerated particles of metal are broken down to 6-8  $\mu$ .<sup>100</sup>

In addition to molded articles, polyacrylic acid derivatives have found application in preparing lacquers, varnishes and other coating compositions. Acrylic

<sup>86</sup> H. Wessenthal, *Kunststoffe*, 1934, 24, 104.

<sup>87</sup> French P. 724,002, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4929.

<sup>88</sup> French P. 666,366, 1928, to Röhm & Haas A.-G.; *Chem. Abs.*, 1930, 24, 1477.

<sup>89</sup> British P. 355,712, 1930, to Röhm & Haas A.-G.; *Chem. Abs.*, 1932, 26, 5580. French P. 38,568, 1930, addn. to 666,366; *Chem. Abs.*, 1932, 26, 1078.

<sup>90</sup> French P. 40,311, 1931, addn. to 666,366, to Röhm & Haas A.-G.; *Chem. Abs.*, 1933, 27, 818.

<sup>91</sup> O. Röhm, British P. 613, 1913; *Chem. Abs.*, 1914, 8, 2268.

<sup>92</sup> British P. 371,813, 1930, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 597. French P. 718,930, 1931; *Chem. Abs.*, 1932, 26, 3393.

<sup>93</sup> M. Hagedorn and A. Oesenbrunner, German P. 604,456, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 860. French P. 757,786, 1934; *Chem. Abs.*, 1934, 28, 3198.

<sup>94</sup> O. Röhm and W. Bauer, U. S. P. 1,982,831, Dec. 4, 1934, to Röhm & Haas A.-G.; *Chem. Abs.*, 1935, 29, 528. British P. 340,677, 1929; *Chem. Abs.*, 1931, 25, 4638.

<sup>95</sup> British P. 373,947, 1931, to Röhm & Haas A.-G.; *Brit. Chem. Abs. B*, 1932, 722. French P. 729,640, 1931; *Chem. Abs.*, 1932, 26, 8035.

<sup>96</sup> British P. 395,291, 1933, to Röhm & Haas A.-G.; *Chem. Abs.*, 1934, 28, 270. French P. 750,873, 1923; *Chem. Abs.*, 1934, 28, 1207. Cf. F. B. Dehn, British P. 401,653, 1932; *Brit. Chem. Abs. B*, 1934, 166.

<sup>97</sup> W. Bauer, German P. 596,679, 1934, to Röhm & Haas A.-G.; *Chem. Abs.*, 1934, 28, 5186.

<sup>98</sup> British P. 357,173, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3572.

<sup>99</sup> W. W. Groves, British P. 420,533 and 420,589, 1934, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1935, 163.

<sup>100</sup> British P. 418,006, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1541.

acid forms an active constituent in a polymerization mixture of vinyl compounds, the products of which may be used in making lacquers.<sup>102</sup> Aqueous dispersions said to be useful for coating and impregnating leather, wood, paper and textiles<sup>103</sup> are prepared by polymerizing an aqueous emulsion of methyl acrylate with hydrogen peroxide at 70-95°C. with the addition of a small amount of Turkey-red oil and sodium di-isopropyl-naphthalenesulphonate. Products applicable to a variety of uses result when acrylic esters are polymerized with styrene in the presence of a non-solvent liquid and a peroxide polymerization catalyst.<sup>104</sup> For example, a mixture of styrene and butyl acrylate along with toluene and benzoyl peroxide polymerizes to yield a viscous solution which may be utilized without further treatment for coating purposes or for the preparation of lacquers. Mixed polymerization products of vinyl ethers with acrylic esters, amides, anilides or nitriles have found use as binding agents and in the manufacture of varnishes and lacquers. Also in admixture with fillers, fabrics and pigment, substitutes for oilcloth, leather and linoleum may be produced.<sup>104</sup>

Printing inks<sup>105</sup> have been described in which a water-soluble coloring matter is added to an aqueous dispersion of amorphous polymers. A typical ink consists of Diamond Green G, glycerol, thioglycol, alcohol, starch and the sodium salt of polyacrylic acid.

Polymerized acrylic esters are stated to render fabrics impermeable to gases, thus producing a useful material for the manufacture of gas masks.<sup>106</sup> Synthetic resins of practical importance have been produced by condensing polyacrylic acid with organic hydroxy compounds.<sup>107</sup> Waterproofing of fibrous materials is said to be accomplished by immersing the cloth in a solution of the ammonium salt of polyacrylic acid and subsequently treating the fabric with a solution of aluminum acetate to form an insoluble salt of the polymer.<sup>108</sup> Water-soluble salts of polyacrylic acid may also find use in the preparation of photographic films.<sup>109</sup>

#### HALOGEN SUBSTITUTION PRODUCTS OF ACRYLIC ACID

Monobromo derivatives of acrylic acid may be obtained from  $\alpha$ - and  $\beta$ -dibromopropionic acids by elimination of a molecule of hydrogen bromide.  $\alpha$ -Monobromoacrylic acid may be so prepared by subjecting  $\alpha$ -dibromopropionic acid to treatment with alcoholic potash with subsequent addition of sulphuric acid to liberate the free acid. The product slowly loses hydrogen bromide on standing to give a soft brownish mass.<sup>110</sup> In a similar manner,  $\beta$ -bromoacrylic acid may be derived from the corresponding  $\beta$ -dibromopropionic acid.<sup>111</sup>

Wagner and Tollens<sup>112</sup> observed that a yellow gelatinous substance was obtained when  $\beta$ -bromoacrylic acid was heated with alcoholic potash. The dried product is insoluble in alcohol, ether and water, although a pronounced swelling of the

<sup>102</sup> British P. 313,569, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1236. French P. 676,424, 1929; *Chem. Abs.*, 1930, 24, 2846.

<sup>103</sup> British P. 387,738, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4700.

<sup>104</sup> H. Fikentscher and W. Wolf, U. S. P. 1,933,052, Oct. 31, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 592. British P. 371,396, 1933; *Chem. Abs.*, 1933, 27, 3570.

<sup>105</sup> British P. 373,643, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3783.

<sup>106</sup> British P. 373,333, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3627.

<sup>107</sup> British P. 373,947, 1930, to Röhm & Haas A.-G.; *Chem. Abs.*, 1933, 27, 3264. For the use of acrylic acid esters on textiles see W. H. Moss, British P. 414,040, 1934, to British Celanese, Ltd.; *Chem. Abs.*, 1935, 29, 357.

<sup>108</sup> A. Voss and E. Dickhäuser, German P. 579,254, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4944.

<sup>109</sup> British P. 371,041, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3914.

<sup>110</sup> French P. 759,449, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3322.

<sup>111</sup> O. Philippi and B. Tollens, *Ann.*, 1874, 171, 333; *J.C.S.*, 1874, 27, 680.

<sup>112</sup> R. Wagner and B. Tollens, *Ann.*, 1874, 171, 340; *J.C.S.*, 1874, 27, 680.

<sup>113</sup> R. Wagner and B. Tollens, *Ann.*, 1874, 171, 355; *J.C.S.*, 1874, 27, 681. M. Garino and G. Bornate (*Gazz. chim. ital.*, 1927, 57, 380; *Chem. Abs.*, 1927, 21, 3600) obtained a pitch when an alcoholic solution of chlorobromopyruvic acid and cinchonine was evaporated.

resinous material takes place in the solvents. Saturation was indicated by the failure of the material to react with bromine or iodine. Complete solution was obtained by using ammonium hydroxide, from which the mass could not be precipitated by the addition of mineral acids. A somewhat similar porous product was obtained by allowing  $\beta$ -bromoacrylic acid to stand over concentrated sulphuric acid. However, the latter polymer differed from the first in that it could be precipitated from its ammoniacal solutions. A third polymeric substance, obtained by treating the potassium salt of the  $\beta$ -bromoacrylic acid with ethyl bromide, was insoluble in ammonium hydroxide. In all three instances, analysis indicated the polymeric formula,  $(C_3H_3O)_n$ .<sup>118</sup>

#### PREPARATION AND POLYMERIZATION OF METHACRYLIC ACID

Lossen and Gerlach<sup>114</sup> used as a starting material for the synthesis of methacrylic acid ( $\alpha$ -methylacrylic acid),  $\alpha$ -bromoisobutyric acid. A yield of 8 per cent of the acid was obtained by splitting off hydrogen bromide with water, 14.8 per cent with 1 *N* sodium hydroxide solution at 80°C., and 75 per cent with 25 per cent alkali. On the other hand,  $\beta$ -bromoisobutyric acid yields only methacrylic acid under all of the foregoing conditions. Methacrylic acid may also be prepared by dehydrating  $\alpha$ -hydroxybutyric acid with phosphorus pentoxide.<sup>115</sup> Crawford<sup>116</sup> synthesized methacrylic acid by heating acetone cyanohydrin in concentrated sulphuric acid at 100-110°C. Polymerization is prevented by the addition of sulphur or diphenylamine.

Methacrylic acid is very susceptible to polymerization.<sup>117</sup> It undergoes polymerization upon distillation, long standing, addition of a few drops of acid or when its aqueous solutions are heated at 130°C. The product obtained in the latter instance is a white porcelain-like mass, insoluble in all neutral solvents. A marked swelling similar to that of gums and starches takes place when the polymer is added to water. The polymerization product is a weak acid which may be dissolved in ammonium hydroxide and reprecipitated with hydrochloric acid. Gummy masses result when its ammoniacal solutions are treated with barium or calcium chloride. According to Mjöen,<sup>118</sup> polymethacrylic acid begins to decompose at 200°C. and volatilizes at 300°C. without melting. Moreover, the polymer is quite resistant to oxidation, being unaffected by potassium permanganate or chromic acid. Titration of this weakly acidic substance with barium hydroxide solution indicates that it is an octabasic acid and in view of the molecular weight estimations, the formula  $(C_4H_5O)_x$  has been proposed, where *x* has a value in the neighborhood of 8.

The zinc and lead salts of methacrylic acid polymerize readily upon heating.<sup>119</sup> The esters of alkylated acrylic acids have been used as sources of resinous products.<sup>120</sup> For example, Fleming and Renfrew<sup>121</sup> used methyl methacrylate and

<sup>112</sup> W. Lossen and E. Kowaki (*Ann.*, 1905, 342, 133; *J.C.S.*, 1906, 90 (1), 59) consider this substance to be polymerized pyruvic acid, since a syrup obtained by extracting an alkaline solution of the polymer with ether combined with phenylhydrazine to give the phenylhydrazone of pyruvic acid.

<sup>114</sup> W. Lossen and O. Gerlach, *Ann.*, 1905, 342, 112; *J.C.S.*, 1906, 90 (1), 61.

<sup>115</sup> French P. 747,068, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 4263.

<sup>116</sup> J. W. C. Crawford, British P. 405,699, 1932, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1934, 313.

<sup>117</sup> R. Fittig and E. Engelhorn, *Ann.*, 1886, 200, 65; *J.C.S.*, 1886, 38, 378.

<sup>118</sup> J. A. Mjöen, *Ber.*, 1897, 30, 1237; *J.C.S.*, 1897, 72, (1), 399.

<sup>119</sup> W. Lossen and O. Gerlach, *loc. cit.*

<sup>120</sup> W. Chalmers, Canadian P. 314,116, 1931; *Chem. Abs.*, 1931, 25, 5177. For the preparation of esters of methacrylic acid see J. W. C. Crawford, British P. 410,308, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 4157. British P. 419,487, 1934; *Brit. Chem. Abs. B*, 1935, 52. W. Cocker, J. S. H. Davies and R. Hill, British P. 406,735, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 4157.

<sup>121</sup> J. S. B. Fleming and A. Renfrew, British P. 398,189, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 1493. A. Renfrew, British P. 398,555, 1933; *Chem. Abs.*, 1934, 28, 1493. See also H. T. Neher and C. S. Hollander, U. S. P. 1,967,323, Nov. 22, 1933, to Rohm & Haas A.-G.; *Chem. Abs.*, 1934, 28, 1160.



products obtained by polymerizing mixtures of methyl acrylate and ethyl methacrylate in the manufacture of an adhesive to be used in the production of laminated glass. Plastic products of commercial significance may be obtained by polymerizing methyl methacrylate by exposure to light and heat, using an organic peroxide or ozonide as a catalyst.<sup>122</sup> In this manner a thermoplastic resin has been prepared which softens only above 100°C. and can set within a small temperature range from a moldable to a rigid, solid condition.<sup>123</sup> Plasticizing agents, fillers and insoluble coloring matter are milled with the acrylic acid derivatives prior to polymerization. The resulting polymer is powdered and molded under pressure (200 pounds per square inch) at 80-200°C. The ethyl ester of methyl acrylic acid, also, yields plastic resins under somewhat similar conditions.<sup>124</sup> In one instance the polymerization is carried out by means of heat or light and with the aid of a benzoyl peroxide catalyst. The resulting polymers are softened by the addition of dibutyl tartrate and dissolved in ethyl acetate. Evaporation of the solvent leaves a film of such character as to recommend it as a boiler-lining or for protective coatings in general.

Before painting rubber surfaces, Münzinger<sup>125</sup> suggests applying an intermediate coating of a polymethacrylic ester in benzene solution (containing a softening agent and rubber). When methacrylonitrile is polymerized alone or with such substances as methyl methacrylate, bubble-formation or distortion due to contraction on cooling is obviated by using a vessel provisionally prepared with a flexible rubber or metal-foil lining.<sup>126</sup>

#### RESINOUS PRODUCTS FROM CROTONIC ACID DERIVATIVES

Crotonic acid ( $\beta$ -methylacrylic acid) does not polymerize as readily as methacrylic acid to give resins,<sup>127</sup> but its esters and other derivatives form useful polymers. Schmidt<sup>128</sup> reports that the polymers of crotonic acid have been obtained in varying degrees of hardness. They are colorless, light-stable and compatible with natural and synthetic resins, plasticizers and most cellulose esters and ethers. Crotyl cellulose in combination with a drying agent may be used in the preparation of lacquers.<sup>129</sup> The film of crotyl cellulose may be polymerized by baking or by exposure to ultraviolet light. Cellulose crotyl esters readily polymerize and have been recommended for use in the manufacture of lacquers, coating compositions, plastic masses, artificial filaments and splinterless glass.<sup>130</sup> Fordyce<sup>131</sup> produced a sheet of solvent-resistant material by treating cellulose tricotinate for 5 hours with intense ultraviolet light or heating at 100°C. for 24 hours. Crotonic acid undergoes condensation and subsequent polymerization when treated with olefins at a temperature of 160°C. Synthetic resins of varied usefulness are said to be produced in this manner.<sup>132</sup> Glycerol can be esterified wholly or partially with crotonic acid to give products which have been added to resins, gums and

<sup>122</sup> R. Hill, British P. 395,687, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 23, 591. French P. 746,713, 1933; *Chem. Abs.*, 1933, 27, 4640. French P. 745,085, 1933; *Chem. Abs.*, 1933, 27, 4363. See also A. Eichengrün, British P. 373,995, 1932, to Cellon-Werke; *Chem. Abs.*, 1933, 27, 3587.

<sup>123</sup> R. Hill, U. S. P. 1,980,432, Nov. 13, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 253.

<sup>124</sup> British P. 401,653, 1933, to Röhm & Haas A.-G.; *Chem. Abs.*, 1934, 28, 2360.

<sup>125</sup> W. M. Münzinger, French P. 770,410, 1934; *Chem. Abs.*, 1935, 29, 641.

<sup>126</sup> L. V. D. Scornah and J. Wilson, British P. 417,999, 1933, to Triplex Safety Glass Co., Ltd.; *Brit. Chem. Abs.*, B, 1935, 12.

<sup>127</sup> R. Stoermer and E. Robert (Ber., 1922, 55, 1030) observed that the transformation of crotonic into isocrotonic acid under the influence of ultraviolet light was accompanied by marked resinification.

<sup>128</sup> H. Schmidt, *Gummi-Ztg.*, 1934, 48, 659; *Brit. Chem. Abs.*, B, 1934, 725.

<sup>129</sup> H. B. Dykstra, U. S. P. 1,929,397, Aug. 1, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 4943.

<sup>130</sup> British P. 391,171, 1933, to British Celanese, Ltd.; *Chem. Abs.*, 1933, 27, 4937.

<sup>131</sup> R. Fordyce, U. S. P. 1,973,493, Sept. 11, 1934, to Eastman Kodak Co.; *Chem. Abs.*, 1934, 28, 7013.

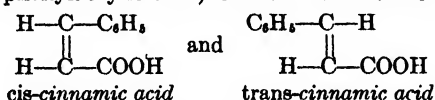
<sup>132</sup> French P. 742,303, 1933, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1933, 27, 3730.

waxes to modify their properties. The crotonic-glycerol esters may also replace camphor in nitrocellulose plastics.<sup>128</sup>

Skraup and Beng<sup>124</sup> have reported that the phenyl ester of  $\beta$ -methylcrotonic acid resinifies on heating at a temperature of 320-330°C. Certain vinylene homologues of crotonic acid esters have been observed to undergo polymerization. Thus Kuhn and Hoffer<sup>129</sup> found that the methyl ester of 2,4,6-octatrienic acid polymerized on long standing to a viscous, yellow, gum-like mass. Also, methyl 3-hydroxy-3-methyl-4,6-octadienate autoxidizes in air to give a viscous syrup. A similar product was obtained from the methyl ester of  $\beta$ -methyloctatrienic acid.

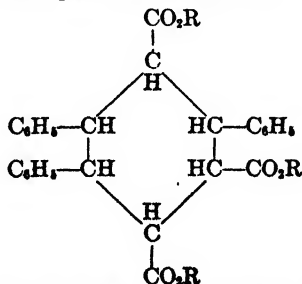
#### POLYMERIZATION OF CINNAMIC ACID AND RELATED COMPOUNDS

Cinnamic acid ( $\beta$ -phenylacrylic acid) exists in two isomeric forms, namely,



The trans-configuration has been assigned to ordinary cinnamic acid. Long ultra-violet rays (e.g., sunlight) favor polymerization whereas shorter rays (mercury arc ray) hinder it. In general the irradiation of cinnamic acids results in isomerization rather than polymerization, and when polymerization does take place, it usually stops at the formation of saturated dimers.<sup>130</sup> However, Stobbe and Lehfelddt<sup>137</sup> reported that nearly a 60 per cent yield of resin was obtained when  $\beta$ -trans-cinnamic acid was subjected to winter sunlight for 5 months. Also, after 4 weeks exposure to summer sunshine, 20 per cent of resinous material was found present.<sup>138</sup>

The esters of cinnamic acid are more prone to polymerization than the acid itself. Liebermann and Zsuffa<sup>139</sup> examined the polymerization tendencies of the methyl, ethyl, isoamyl, benzyl and allyl esters of cinnamic acid by exposing the esters to the influence of ultraviolet light or sunlight. The ethyl ester was found to polymerize most readily followed by the isoamyl ester. However, in general the yields were quite low, being only from 3 to 6 per cent in the case of ethyl cinnamate. Favorable conditions for polymerization involved distillation of the ester, followed by exposure to light for a long period of time with subsequent heat treatment at 85-90°C. for 10-20 hours. The products as obtained were white, infusible, odorless and sparingly soluble. A study of the properties of the polyesters indicated a trimer of the possible constitution



<sup>128</sup> French P. 766,693, 1934, to Soc. des usines chimiques Rhône-Poulenc; *Chem. Abs.*, 1934, 28, 7444.

<sup>129</sup> S. Skraup and E. Beng, *Ber.*, 1927, 60, 944; *Chem. Abs.*, 1927, 21, 2125.

<sup>130</sup> R. Kuhn and M. Hoffer, *Ber.*, 1930, 63, 2164; *Chem. Abs.*, 1931, 25, 683. *Ber.*, 1932, 65, 646; *Chem. Abs.*, 1932, 26, 3497.

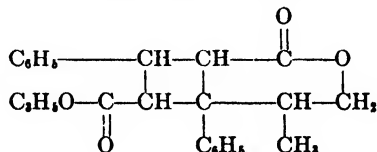
<sup>137</sup> For a more complete discussion of the action of ultraviolet light on cinnamic acids, see Carleton Ellis and A. A. Wells, "The Chemical Action of Ultraviolet Rays," Chemical Catalog Co., New York, 1925, 178.

<sup>138</sup> H. Stobbe and A. Lehfelddt, *Ber.*, 1925, 58, 2415; *Chem. Abs.*, 1926, 20, 1066.

<sup>139</sup> H. Stobbe, G. Ljungren, and J. Freyberg, (*Ber.*, 1926, 59, 270) made the observation that considerable resin formation takes place during the synthesis of dibenzylsuccinic acid.

<sup>140</sup> C. Liebermann and M. Zsuffa, *Ber.*, 1911, 44, 841; *Chem. Abs.*, 1911, 5, 2280.

On the other hand, when polymerization is carried out by special heat treatment alone, different types of polymers are obtained.<sup>140</sup> Heat polymerization of allyl cinnamate yields two different polymers, depending upon the reaction time. Polymer A was obtained in 25 per cent yield when the ester was heated in a sealed tube at 210°C. for 6 hours; a 60 per cent yield of polymer B resulted when the heating time was extended to 15 hours. The heat-polymers differ in several respects from the corresponding light-polymers. For example, the heat-polymers may be hydrolyzed with 40 per cent aqueous alkali or 25 per cent alcoholic alkali, whereas the light-polymers are quite resistant to hydrolysis. The following structure has been assigned to the heat-polymer of allyl cinnamate:



Polymerized methyl cinnamate is recommended as an adhesive material for the preparation of unsplinterable glass.<sup>141</sup> The polymerization is effected by either heat or light. According to Ostromislensky<sup>142</sup> the polymerized esters of phenylacrylic acid are particularly adaptable for the manufacture of non-shattering glass because of their permanent clear, colorless transparency and their high refractive indices. Amyl, amylene, isopropyl, butylene and isobutylene esters of phenylacrylic acid may be polymerized by heat or exposure to ultraviolet light. Chlorobenzene, ethylene bromide or similar solvents have been used in preparing adhesives. The ethyl and methyl esters are also said to be effective when used in conjunction with cellulose esters.<sup>143</sup> An amber-colored varnish resin may be prepared by heating allyl cinnamate for 36 hours at 170°C. in a closed enamelled vessel, after which the temperature is raised to 230°C. and maintained for an additional 36 hours.<sup>144</sup> Skraup and Beng<sup>145</sup> have reported that the phenyl ester of cinnamic acid shows evidence of considerable resinification when heated in a sealed tube for 25 hours at 290-300°C.

Cinnamalacetic acid  $\text{C}_6\text{H}_5\text{—CH=CH—CH=CH—COOH}$ , according to Liebermann and Riiber,<sup>146</sup> yields liquid polymeric modifications of phenylbutadiene when heated with barium hydroxide. Blicke<sup>147</sup> polymerized the allyl ester of cinnamalacetic acid by heating it in a sealed tube at 210°C. for 7 days. At the end of this time the solid, light-yellow, transparent mass was dissolved in warm acetone, filtered and cooled to 0°C. The polymer was isolated by pouring the acetone solution into a large volume of cold alcohol. The purified polymeric ester was obtained in 25 per cent yield as an amorphous, amber-like solid. A small yield of a white, gummy substance was obtained with this ester upon exposure to sunlight for several days. The nature of the product was not investigated, but it is believed to be analogous to the light-polymers obtained by Liebermann<sup>148</sup> and

<sup>140</sup> C. Liebermann and M. Kardos, *Ber.*, 1913, 46, 1055; *Chem. Abs.*, 1913, 7, 2554.

<sup>141</sup> British P. 297,413, 1927, to Röhm & Haas A.-G.; *Chem. Abs.*, 1929, 23, 2797. French P. 654,357, 1928; *Chem. Abs.*, 1929, 23, 3785.

<sup>142</sup> I. Ostromislensky, U. S. P. 1,913,127, June 6, 1933, to Naugatuck Chemical Co.; *Chem. Abs.*, 1933, 27, 4368.

<sup>143</sup> L. J. B. Forbes and W. B. Price, British P. 406,644, 1932, to Triplex (Northern), Ltd.; *Brit. Chem. Abs. B*, 1934, 414. British P. 375,972, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3575.

<sup>144</sup> A. Kronstein, U. S. P. 843,401, Feb. 5, 1907; *Chem. Abs.*, 1907, 1, 918. A balsam can be prepared from allyl malonate by heating for 24 hours in a similar vessel.

<sup>145</sup> S. Skraup and E. Beng, *Ber.*, 1927, 60, 945.

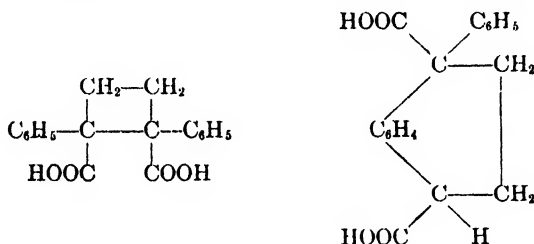
<sup>146</sup> C. Liebermann and C. N. Riiber, *Ber.*, 1900, 33, 2400; 1902, 35, 2096. O. Doebner and H. Standinger, *ibid.*, 1903, 36, 4318.

<sup>147</sup> F. F. Blicke, *J.A.C.S.*, 1923, 17, 1562.

<sup>148</sup> C. Liebermann and C. N. Riiber, *Ber.*, 1900, 33, 2400; 1902, 35, 2096.

his co-workers. Clemo, Haworth and Walton<sup>140</sup> found that  $\beta$ -4-methoxy-2,5-dimethylbenzoylacrylic acid was converted into a tarry mass when heated to 100°C. Also another substituted acrylic acid, 3,5-dimethyl-4-carbethoxy-pyrrol-2-acrylic acid, was obtained in the form of a resinous dark brown, glassy mass upon heating to 200°C.<sup>140</sup> The product is insoluble in ether, but dissolves readily in alcohol and acetone.

Atropic acid ( $\alpha$ -phenylacrylic acid) also seems to be capable of exhibiting cis-trans isomerism.<sup>151</sup> Dimers, bearing the same relation to atropic acid as the truxillic acids do to cinnamic acid, were obtained by protracted fusion or heating aqueous solutions. Possible constitutional formulas for the two isotropic acids were proposed by Fittig.<sup>152</sup>



Baker and Eccles<sup>153</sup> observed that the methyl ester of atropic acid polymerized after standing.

#### VINYLACRYLIC ACID AND ITS DERIVATIVES

Polymeric modifications of  $\beta$ -vinylacrylic acid were observed by Doebner<sup>154</sup> to form slowly when the acid was allowed to stand at room temperature. However, the transformation took place rapidly when the acid was heated at 130°C., yielding an amorphous, brittle product of the formula  $(C_5H_6O_2)_x$ . The polymer is insoluble in organic solvents with the exception of acetic acid, in which solution occurs with difficulty at the boiling temperature. The resin may be dissolved by heating in a sodium hydroxide solution; however, solutions of sodium carbonate have very little solvent action. Decomposition of the polymer takes place at 300°C. A white, rubber-like polymer was prepared by Burton and Ingold<sup>155</sup> during the crystallization of crude vinylacrylic acid from water between 55° and 15°C. The yield of polymer thus obtained increased with the time of crystallization. The fact that esters of vinylacrylic acid readily absorb oxygen from the air to form tough films has suggested their use as a substitute for linseed oil.<sup>156</sup>

Halogen-substitution products of vinylacrylic acid are relatively unstable and undergo polymerization quite easily. Muscat and Becker<sup>157</sup> have reported that a sharp melting point for chlorovinylacrylic acid is not obtainable because of its ready polymerization. The polymer obtained from this acid is a light yellow solid, soluble in acetone, but insoluble in other ordinary organic solvents. Simi-

<sup>140</sup> G. R. Clemo, R. D. Haworth, and E. Walton, *J.C.S.*, 1929, 2382.

<sup>150</sup> W. Kilster, E. Brudi and G. Koppenhöfer, *Ber.*, 1925, 58, 1014.

<sup>151</sup> C. Liebermann, *Ber.*, 1895, 28, 137; *J.C.S.*, 1895, 68, 225.

<sup>152</sup> R. Fittig, *Ann.*, 1881, 206, 34; *J.C.S.*, 1881, 40, 425.

<sup>153</sup> J. W. Baker and A. Eccles, *J.C.S.*, 1927, 2318.

<sup>154</sup> O. Doebner, *Ber.*, 1902, 35, 1137.

<sup>155</sup> H. Burton and C. K. Ingold, *J.C.S.*, 1929, 2028.

<sup>156</sup> L. Rosenthal and L. Taub, German P. 389,086, 1922, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1924, 43, 434B.

<sup>157</sup> I. E. Muscat and B. C. Becker, *J.A.C.S.*, 1930, 52, 812.

larly, monobromovinylacrylic acid is very susceptible to polymerization.<sup>158</sup> When this substance was heated it changed without melting or evident degradation to a yellow, apparently amorphous solid, which gradually darkened in color as the temperature rose. Bromovinylacrylic acid cannot be kept, since it invariably goes over to a brown, amorphous mass in less than 2 days. The methyl ester of bromovinylacrylic acid polymerizes to a thick jelly on standing for two hours at room temperature.<sup>159</sup> Muscat and Hudson<sup>160</sup> obtained what appeared to be a polymer of 3-chlorovinylacrylic acid by shaking an ethereal solution of vinylacrylic acid chlorohydrin with phosphorus pentoxide.

#### RESINOUS POLYMERS FROM ESTERS OF ITACONIC ACID

Itaconic acid  $\text{CH}_2=\text{C}-\underset{\text{COOH}}{\text{CH}_2}-\text{COOH}$  has found little or no use as a source of

resinous polymers.<sup>161</sup> However, its esters yield various products upon polymerization, some of which are of special technical significance. In general, earlier investigators have reported the polymerization of dialkyl esters of itaconic acid to be quite slow. Swartz<sup>162</sup> observed that diethyl itaconate was converted, on long standing, to a solid, glass-like modification. Anschütz<sup>163</sup> prepared a similar product by allowing the sample of itaconic ester to stand for 19 months (in order to ensure complete polymerization). The slowness of these reactions was also confirmed by Fittig and Bock,<sup>164</sup> who found, in addition, that polymerization did not occur at all in the presence of ethyl alcohol. Amyl itaconate also undergoes polymerization to yield a glass-like polymer.<sup>165</sup>

A thorough investigation of the effect of light on the polymerization of ethyl itaconate was carried out by Stobbe and Lippold.<sup>166</sup> The course of the polymerization was followed by periodic measurements of the refractive index. The pure ester, whose index of refraction was 1.43609, was converted after 65 days of exposure to sunlight into an amorphous polymer, giving the crude mixture a refractive index of 1.44928. Light seems to be an essential factor in the conversion, for a similar preparation in the dark remained unchanged. In addition to the light, traces of hydrogen chloride were said to increase the rate of reaction. The polymer, as obtained, is an odorless, colorless, glassy substance which dissolves in the monomeric ester to form a viscous liquid. The polymer cannot be distilled, since even *in vacuo* it decomposes, yielding volatile products.

Extensive experiments dealing with the conditions of polymerization have enabled Hope<sup>167</sup> to produce desirable polymers without recourse to light-exposure. Provided anticatalytic phenomena were avoided, it was found possible to accelerate the reaction to a marked extent by heating. The polymerized ester has found application in the manufacture of laminated glass. A partially polymerized paste is applied to a sheet of cellulose acetate, which is then placed

<sup>158</sup> I. E. Muscat, B. C. Becker and J. S. Lowenstein, *J.A.C.S.*, 1930, 52, 326.

<sup>159</sup> E. H. Farmer and A. T. Healey, *J.C.S.*, 1927, 1060.

<sup>160</sup> I. E. Muscat and L. Hudson, *J.A.C.S.*, 1931, 53, 3178.

<sup>161</sup> Y. Volmar (*Compt. rend.*, 1925, 181, 467; *Chem. Abs.*, 1926, 20, 369) has studied the effect of ultraviolet light on itaconic acid.

<sup>162</sup> Swartz, *Jahresber.*, 1873, 579.

<sup>163</sup> R. Anschütz, *Ber.*, 1881, 14, 2787.

<sup>164</sup> R. Fittig and V. Bock, *Ann.*, 1904, 331, 174; *J.C.S.*, 1904, 86 (1), 745.

<sup>165</sup> P. Walden, *Z. physik. Chem.*, 1896, 20, 382; *J.C.S.*, 1896, 70 (2), 633.

<sup>166</sup> H. Stobbe and A. Lippold, *J. prakt. Chem.*, 1914, (3) 90, 336; *J.C.S.*, 1915, 108 (1), 213.

<sup>167</sup> E. Hope, U. S. P. 1,644,131, Oct. 4, 1927, to F. W. Atack; *Chem. Abs.*, 1927, 21, 4040. See also *Plastics*, 1928, 4, 78. British P. 254,668, 1925; *Brit. Chem. Abs. B*, 1926, 747. British P. 264,550, 1925; *Chem. Abs.*, 1928, 22, 91. F. W. Atack, German P. 484,146, 1928; *Chem. Abs.*, 1930, 24, 938. The use of polymerized esters of itaconic, acrylic, and crotonic acids in the manufacture of safety glass is discussed in *Plastic Products*, 1934, 10, 131.

between two sheets of glass and heated for 3 days at 70°C. to complete the polymerization. Vitreous masses which may be molded are obtained in a similar manner.

Polymerized itaconic acid has been recommended as a constituent of modified resins. When mixed with a urea-formaldehyde condensation product, resins said to be useful in the manufacture of varnishes, films, artificial silk and molded articles have been obtained.<sup>168</sup> Jaeger<sup>169</sup> has described a resinous product (which can be molded and polished), obtained by adding polymerized itaconic acid to a phthalide-modified alkyd resin.<sup>170</sup> Media for the dispersing of insoluble substances can be made from derivatives of polymeric itaconic acid mixed with complex polymerization products obtained by simultaneous condensation and polymerization of vinyl compounds.<sup>171</sup> When dissolved in water, either alone or mixed with starch, dextrin or gum arabic, the viscous masses may be used for dispersing dyes or pigments. The viscous preparation may also be employed in the manufacture of printing pastes, printing inks, coating preparations and colloidal pastes of coloring materials.

The polymers of itaconic acid and its esters (as well as acrylic acid and its esters, vinyl alcohol esters and ethers, and styrene) have been suggested as material for the manufacture of phonograph records.<sup>172</sup>

<sup>168</sup> British P. 309,487, 1929, to Kunsthartzfabr F. Pollak G.m.b.H.; *Chem. Age (London)*, 1929, 20, 571. See also Chapter 32.

<sup>169</sup> A. O. Jaeger, U. S. P. 1,800,098, May 24, 1932, to Selden Co.; *Chem. Abs.*, 1932, 26, 3945. U. S. P. 1,941,474, Jan. 2, 1934; *Chem. Abs.*, 1934, 28, 1880.

<sup>170</sup> A description of this is found in Chapter 45.

<sup>171</sup> British P. 369,915, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3046.

<sup>172</sup> British P. 409,550, 1934, to Consortium für elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1934, 28, 6259.

## Chapter 54

### Resins from Rubber

#### I. General Considerations

##### STRUCTURE OF RUBBER

Mention has already been made of the very intimate relationship existing between resins and rubber-like substances.<sup>1</sup> Heat and certain chemical reagents convert rubber into resinous bodies. The exact formulation of the changes which take place is not known, but fairly definite concepts as to the transformations involved may be based on the assumed structure of rubber.

Rubber<sup>2</sup> is an emulsoid consisting of the colloidal hydrocarbon rubber in a fine state of subdivision; the rubber not only forms the disperse phase but also its own dispersion medium. The impurities in crude rubber consist of resins, proteins, carbohydrates and enzymes and may be removed if necessary by dissolving the rubber in an appropriate solvent and precipitating.<sup>3</sup> As is the case with most gels, there is first a swelling of the rubber and absorption of the solvent resulting in a colloidal solution of high viscosity.<sup>4</sup>

The purified rubber reveals on analysis the empirical formula,  $C_5H_8$ . The general properties indicate a much more complex molecule. The structure of rubber is based on the following considerations: 1, the close relationship between isoprene and rubber; 2, the decomposition products of rubber ozonides; and 3, the formation of addition compounds.

Of the changes which rubber undergoes, the most instructive, at least from the historical point of view, are those arising from destructive distillation. A systematic study of the distillation products was very early undertaken by Bouchardat<sup>5</sup> and later by Williams.<sup>6</sup> The latter obtained a liquid (boiling at 37°C.) having the formula,  $C_5H_8$ , to which he gave the name "isoprene." Before any elucidation of the structure of rubber might arise, it was necessary to know the constitution of isoprene. Tilden,<sup>7</sup> on purely empirical grounds considered it to be 2-methyl butadiene and the correctness of this contention was established by Kondakov,<sup>8</sup> by Ipatiev and Wittorf<sup>9</sup> and by Euler.<sup>10</sup>

Dipentene was also found in the products of the destructive distillation of rubber and its mode of formation is readily explained by a simple union of two isoprene molecules

<sup>1</sup> See Chapters 4 and 9.

<sup>2</sup> For an extensive discussion of rubber, its sources, structure, physical properties and chemical transformations, see K. Memmler, "The Science of Rubber," trans. by R. F. Dunbrook and V. N. Morris, Reinhold Publishing Corp., New York, 1934.

<sup>3</sup> F. Heim and R. Marquis, *Bull. de l'Office Colonial*, 1915, 8 (86), 101; *J.S.C.I.*, 1915, 34, 1062.

<sup>4</sup> The colloidal changes involved in vulcanisation and the action of copper salts on raw rubber have been discussed by I. Williams (*Ind. Eng. Chem.*, 1934, 26, 1190) and by B. V. Buisov, V. S. Molodenakii and N. I. Mikhailov (*Kautschuk*, 1934, 10, 86, 104; *Chem. Abs.*, 1934, 28, 6589) respectively.

<sup>5</sup> A. Bouchardat, *J. de Pharmacie*, 1837, 23, 457.

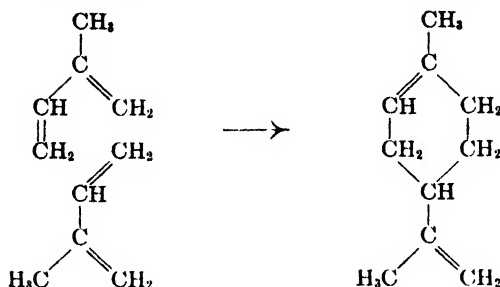
<sup>6</sup> G. Williams, *Proc. Roy. Soc.*, 1880, 10, 516.

<sup>7</sup> W. A. Tilden, *Chem. News*, 1883, 46, 120; *J.C.S.*, 1883, 44, 75.

<sup>8</sup> I. Kondakov, *J. Russ. Chem. Soc.*, 1883, 20, 706; 1889, 21, 80; *J.C.S.*, 1889, 56, 1127.

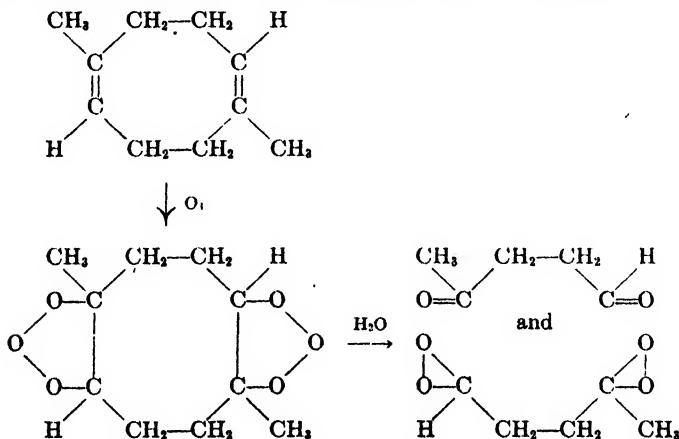
<sup>9</sup> W. Ipatiev and N. von Wittorf, *J. prakt. Chem.*, 1897, (3) 53, 1; *J.C.S.*, 1897, 72 (1), 233.

<sup>10</sup> W. Euler, *Ber.*, 1897, 30, 1989.

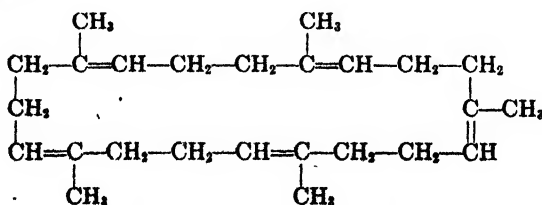


Although dipentene is the chief product in the distillation of rubber, opinion is divided as to whether it arises from a primary or secondary process, that is from rubber or from isoprene.

Further evidence regarding the structure of rubber came from ozonolysis. When ozone is passed into a chloroform solution of rubber, an ozonide is formed which can be isolated as a vitreous mass and purified by solution in ethyl acetate and subsequent precipitation with petroleum ether. Analysis of the ozonide revealed the composition  $(C_5H_8O_3)_x$ , further evidence for a double bond for each 5-carbon moiety.<sup>11</sup> When heated with water the ozonide decomposed into hydrogen peroxide, levulinic aldehyde and levulinic aldehyde peroxide, which in turn further decomposed into levulinic acid. In that the molecular formula corresponds to  $C_{10}H_{16}O_6$ , Harries<sup>12</sup> concluded that the structure of rubber was that of polymerized 2,6-dimethyl-1,5-cyclo-octadiene. The reactions may be represented as follows:



Harries<sup>13</sup> later modified his views and wrote the structure of the rubber molecule as  $(C_5H_8)_x$  or  $C_{2x}H_{10}$ :



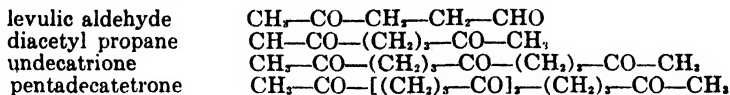
<sup>11</sup> C. D. Harries, *Ber.*, 1904, 37, 2708; *J.C.S.*, 1904, 86 (1), 757.

<sup>12</sup> C. D. Harries, *Ber.*, 1905, 38, 1195; *J.C.S.*, 1905, 88 (1), 364.

<sup>13</sup> C. D. Harries, *Ann.*, 1914, 406, 173; *Chem. Abs.*, 1915, 9, 283.

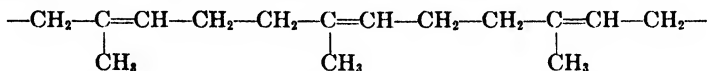


This structure is based on the fact that  $\alpha$ -isocaoutchouc<sup>14</sup> forms an ozonide which on decomposition yields



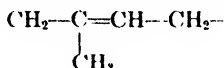
and the corresponding acids. The caoutchouc molecule is thus considered as built up of a 20-carbon ring containing 5 olefin linkages.

Pickles<sup>15</sup> considered rubber to be a long chain built up of isoprene units by 1,4 conjugation, with the ends joined to form a closed ring:



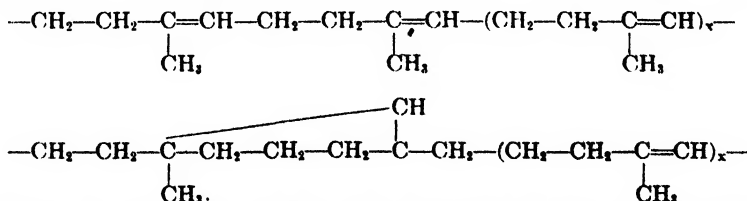
The number of isoprene units was uncertain but it was postulated to be in the neighborhood of eight.

A series of investigations on the structure of natural rubber were carried out by Midgley and Henne.<sup>16</sup> The destructive distillation of crepe rubber yielded largely isoprene, dipentene and heveen ( $\text{C}_{16}\text{H}_{24}$ ) together with other hydrocarbons in smaller quantity. The compounds which were identified consisted of molecules which could easily have been derived from the rubber unit



by the processes of hydrogenation, dehydrogenation, double-bond migration or auto-addition. In the case of sodium rubber (prepared by boiling isoprene with liquid sodium-potassium alloy) pyrolysis gave a decreased yield of the unsaturated compounds, isoprene and dipentene, an increased amount of pentenes and a small amount of saturated hydrocarbons.<sup>17</sup> The last were entirely absent in the natural-rubber distillate. The destructive distillation of ebonite yielded 2-methylthiophene, 2,3-dimethylthiophene, 2,4-dimethylthiophene, 2,5-methylethylthiophene and m-xylene.<sup>18</sup>

When rubber itself is heated in a vacuum the macromolecules decompose into residues of 20-50 isoprene units, which in turn form polycyclorubber, and into smaller residues which form isoprene, dipentene and sesquiterpenes.<sup>19</sup> A similar cyclorubber can be obtained by the destructive distillation of rubber in a stream of carbon dioxide under atmospheric pressure. Other products obtained consist of dipentene, isoprene and hexadiene. Dipentene occurs in the greatest quantity. These products are not only decomposition products of rubber but also of the polycyclorubber. The change of normal to cyclorubber can be represented thus:



<sup>14</sup>  $\alpha$ -Isocaoutchouc is the product obtained by removal of the halogen acid from the rubber hydracid by means of bases; it is not identical with ordinary caoutchouc. See Chapter 55.

<sup>15</sup> S. S. Pickles, *J.C.S.*, 1910, 97, 1088.

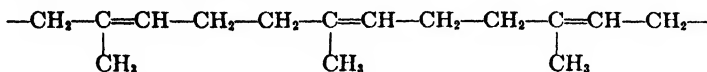
<sup>16</sup> T. Midgley, Jr., and A. L. Henne, *J.A.C.S.*, 1929, 51, 1215; 1931, 53, 203. T. Midgley, Jr., A. L. Henne and M. W. Renoll, *ibid.*, 1931, 53, 2733; 1932, 54, 3343, 3381.

<sup>17</sup> T. Midgley, Jr., A. L. Henne and A. F. Shepard, *J.A.C.S.*, 1932, 54, 381.

<sup>18</sup> T. Midgley, Jr., A. L. Henne and A. F. Shepard, *J.A.C.S.*, 1932, 54, 2953.

<sup>19</sup> H. Staudinger and W. Widmer, *Helv. Chim. Acta*, 1926, 9, 529; *Chem. Abs.*, 1926, 20, 3587. H. Staudinger and E. Geiger, *Helv. Chim. Acta*, 1926, 9, 549; *Chem. Abs.*, 1926, 20, 3588.

Staudinger and his co-workers<sup>20</sup> have brought forth a mass of evidence to show that rubber is built up of long chains of conjugated isoprene units with the formation of a linear polymeric structure.



The average weight of the rubber molecule is exceedingly large—perhaps as high as 70,000.

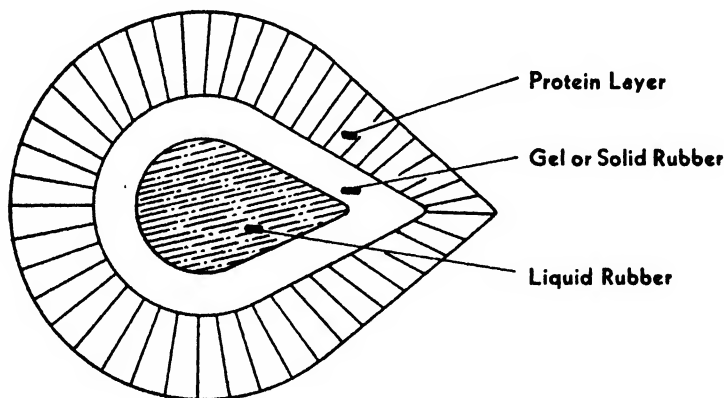


FIG. 140.— Latex Particle.

The commonest dispersion of rubber is the naturally occurring emulsion known as latex. The latter is secreted in small vessels and sacs located in the cortical tissue of plants belonging to the orders *Euphorbiaceae*, *Urticaceae*, *Apocynaceae* and *Asclepiadaceae*. The rubber is found in small globules suspended in a watery fluid which also holds certain proteins, carbohydrates and a small proportion of salts in

<sup>20</sup> H. Staudinger, "Die hochmolekularen organischen Verbindungen," J. Springer, Berlin, 1932, 378. H. Staudinger, *Chem. Ztg.*, 1934, 58, 225; *Chem. Abs.*, 1934, 28, 3615. *Ibid.*, 1932, 45, 276, 292; *Chem. Abs.*, 1932, 26, 3953. For earlier work: H. Staudinger, M. Asano, H. F. Bondy and R. Signer, *Ber.*, 1928, 61, 2575; *Chem. Abs.*, 1929, 23, 2847; *Rubber Chem. Tech.*, 1930, 3, 494. H. Staudinger and H. F. Bondy, *Ann.*, 1929, 468, 1; *Ber.*, 1929, 62, 4211; *Chem. Abs.*, 1929, 23, 3872; 1930, 24, 3129. H. Staudinger and H. F. Bondy, *Ber.*, 1930, 63, 724; *Rubber Chem. Tech.*, 1930, 3, 516; *Chem. Abs.*, 1930, 24, 3130, 4657. H. Staudinger and H. F. Bondy, *Ber.*, 1930, 63, 734; *Rubber Chem. Tech.*, 1930, 3, 519; *Chem. Abs.*, 1930, 24, 3131. H. Staudinger and E. O. Leupold, *Ber.*, 1930, 63, 730; *Rubber Chem. Tech.*, 1930, 3, 516; *Chem. Abs.*, 1930, 24, 3130. H. Staudinger and J. R. Senior, *Helv. Chim. Acta*, 1930, 13, 1321; *Rubber Chem. Tech.*, 1931, 7, 365; *Chem. Abs.*, 1931, 25, 3518. H. Staudinger and W. Schaal, *Helv. Chim. Acta*, 1930, 31, 1355; *Rubber Chem. Tech.*, 1932, 5, 131. H. Staudinger, E. Geiger, E. Huber, W. Schaal and A. Schwalbach, *Helv. Chim. Acta*, 1930, 13, 1334; *Rubber Chem. Tech.*, 1931, 4, 532; *Chem. Abs.*, 1931, 25, 3518. H. Staudinger, M. Brunner and E. Geiger, *Helv. Chim. Acta*, 1930, 13, 1968; *Rubber Chem. Tech.*, 1932, 5, 141; *Chem. Abs.*, 1931, 25, 3519; H. Staudinger and W. Feisst, *Helv. Chim. Acta*, 1930, 13, 1361; *Rubber Chem. Tech.*, 1932, 5, 130; *Chem. Abs.*, 1933, 27, 6016. H. Staudinger, *Ber.*, 1931, 64, 1407; *Rubber Chem. Tech.*, 1932, 5, 263; *Chem. Abs.*, 1931, 25, 5055. H. Staudinger and R. Nodsu, *Helv. Chim. Acta*, 1931, 25, 1350; *Rubber Chem. Tech.*, 1931, 4, 543; *Chem. Abs.*, 1931, 23, 3519. H. Staudinger, H. F. Bondy, J. Joseph and E. O. Leupold, *Ann.*, 1931, 488, 53; *Rubber Chem. Tech.*, 1932, 5, 265; *Chem. Abs.*, 1931, 25, 5796. H. Staudinger and H. F. Bondy, *Ann.*, 1931, 488, 153; *Rubber Chem. Tech.*, 1932, 5, 278; *Chem. Abs.*, 1931, 25, 5796. H. Staudinger and E. O. Leupold, *Helv. Chim. Acta*, 1932, 15, 221; *Rubber Chem. Tech.*, 1932, 5, 576; *Chem. Abs.*, 1932, 26, 2618.

Papers which agree with Staudinger's viewpoint: P. Stamberger and C. M. Blow, *Kolloid-Z.*, 1930, 53, 90; *Brit. Chem. Abs. A*, 1930, 1519. H. Kroepelin, *Kautschuk*, 1930, 6, 158; *Brit. Chem. Abs. B*, 1930, 623. Papers which present other formulas or treat rubber as not containing macromolecules: M. C. Boswell, A. Hambleton, R. R. Parker and R. K. McLaughlin, *Can. Chem. Met.*, 1923, 6, 327; *J.S.C.I.*, 1923, 42, 63A. *India Rubber J.*, 1923, 64, 981; *Chem. Abs.*, 1923, 17, 2655. C. Harries, *Ber.*, 1923, 56, 1048; *Chem. Abs.*, 1923, 17, 2808. H. Loewen, *Kautschuk*, 1931, 7, 12; *Brit. Chem. Abs. A*, 1931, 492. K. Shimada, *J. Chem. Ind. (Japan)*, 1934, 37, 126; *Brit. Chem. Abs. B*, 1934, 685.

General papers on rubber and the action of a number of reagents upon it: K. Asano, *J. Chem. Ind. (Japan)*, 1931, 24, 330; *Chem. Abs.*, 1932, 16, 1168. H. L. Fisher, *Ind. Eng. Chem.*, 1923, 15, 860; 1924, 16, 627. H. R. Thies and A. M. Clifford, *ibid.*, 1934, 26, 123.

solution. If the latex is not to be worked up into rubber directly, ammonia is added to prevent putrefactive changes which otherwise take place and which result in coagulation. If an acid is added, the rubber separates in solid flakes or curds, this being a method commonly employed to obtain rubber. However, heat and astringent plant juices will produce the same effect.

In applying protective films to surfaces, the simplest method is to use a dispersion.<sup>21</sup> For example, a layer of rubber isomer<sup>22</sup> may be deposited on an object from solution followed by a layer of rubber from an aqueous dispersion.<sup>23</sup> The deposited material is then dried and vulcanized. A dispersion of rubber isomer in gasoline or benzene is stated by Geer<sup>24</sup> to produce a film which is resistant to those vapors and gases which corrode metals.<sup>25</sup> Hard-rubber varnishes can be made by dissolving rubber in a volatile solvent and vulcanizing at 125°C.<sup>26</sup> The product is rendered colloidal by heating under pressure at 180°C. Hardened rosin or cumarone resin can be added to increase the ease of application.<sup>27</sup> Shepard and Schmitt<sup>28</sup> have described a quick-drying composition prepared by heating a mixture of devulcanized rubber, rosin and tung oil until homogeneous. Benzene is added to the resultant material as a diluent.

It was pointed out by Smith, Garnett and Dean<sup>29</sup> that an insulating compound may be made by mixing wholly or partially deresinated gutta-percha or balata with petroleum jelly as a softener. Natural or synthetic rubber may also be added. In mixtures containing 15 per cent of petroleum jelly, tendency to sweat is overcome by heating to about 50°C.<sup>30</sup> Purified rubber in conjunction with 1-20 per cent of "Superla wax" (m.p., 71-77°C.), ozokerite or ceresin has been utilized by Kemp and Ingmanson<sup>31</sup> for a similar purpose. The same workers developed a process in which resin is extracted from gutta-percha, separated into alban and fluavil and the former restored to the gutta-percha. High-frequency submarine cables can be insulated with the body formed. Alban from other materials (chicle) may also be added to deresinated gutta-percha and then incorporated in rubber.<sup>32</sup> Cold alcohol is used as a selective solvent for fluavil to accomplish the separation from alban. The addition of as much as 15 volumes of asphalt to 100 volumes of rubber has been reported as improving the physical properties of the latter.<sup>33</sup>

<sup>21</sup> B. Dales, U. S. P. 1,813,440, July 7, 1931, to B. F. Goodrich Co., *Chem. Abs.*, 1931, 25, 5311.

<sup>22</sup> The term "rubber isomer" is applied to the hydrocarbons formed from rubber by the various agencies mentioned later in this chapter. They are less unsaturated than rubber, due probably to the mutual saturation of some of the double bonds to form cyclic structures.

<sup>23</sup> Artificial aqueous dispersions of rubber have been prepared by W. B. Pratt, *British P.* 217,612, 1922; *J.S.C.I.*, 1924, 43, 757B. See also J. B. Tuttle, *India Rubber World*, 1923, 67, 213, 291.

<sup>24</sup> W. C. Geer, U. S. P. 1,744,881, Jan. 28, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 1527. Aqueous emulsions of such solutions have also been utilized as coatings and impregnants. French P. 745,229, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4441.

<sup>25</sup> Hard rubber dust has been included in such coating compositions. H. L. Trumbell, U. S. P. 1,906,437, May 2, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 3639.

<sup>26</sup> H. Plauson, *British P.* 326,216, 1928; *Brit. Chem. Abs. B.*, 1930, 520. See also P. Finley, U. S. P. 146,387, Jan. 13, 1874. W. A. Gibbons and T. V. Binmore (U. S. P. 1,745,533, Feb. 4, 1930, to Mechanical Rubber Co.; *Chem. Abs.*, 1930, 24, 1765) utilized vulcanized scrap rubber by dissolving it in solvent naphtha and heating with sulphur.

<sup>27</sup> L. J. Buttolph (U. S. P. 1,658,476, Feb. 7, 1928; *Chem. Abs.*, 1928, 22, 1244) included anthracene in a fluorescent paint which was similarly composed.

<sup>28</sup> S. E. Shepard and J. J. Schmitt, U. S. P. 1,701,129, Feb. 5, 1929, to Eastman Kodak Co.; *Chem. Abs.*, 1929, 23, 1528. Cf. the preparation of an oil varnish from stand oil, *British P.* 419,611, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1935, 195.

<sup>29</sup> W. S. Smith, H. J. Garnett and J. N. Dean, *British P.* 346,383, 1929; *Chem. Abs.*, 1933, 27, 448.

<sup>30</sup> W. S. Smith, H. J. Garnett and J. N. Dean, *British P.* 326,481, 1928; *Chem. Abs.*, 1930, 24, 4900.

<sup>31</sup> A. R. Kemp and J. H. Ingmanson, *British P.* 353,518, 1930, to Electrical Research Products, Inc.; *Chem. Abs.*, 1933, 27, 448.

<sup>32</sup> A. R. Kemp and J. H. Ingmanson, *British P.* 353,519, 1930, to Electrical Research Products, Inc.; *Chem. Abs.*, 1933, 27, 448.

<sup>33</sup> C. O. North, *Chem. Met. Eng.*, 1922, 26, 253. For a discussion of the various means of incorporating asphalt into rubber, see F. C. van Hourn and M. A. Begheyn, *Kolloid Z.*, 1934, 66, 219; *Chem. Abs.*, 1934, 28, 3943.

Goodenow<sup>34</sup> sprayed finely divided kauri or Manila copal on a thin sheet of uncoagulated latex which was then milled. The product was dissolved in turpentine, naphtha or carbon tetrachloride, evaporated to any desired extent and used as an adhesive. This cement was said to have the elasticity of rubber but much better weathering properties. In a related procedure, a solution of an alkali sulphate, silicate or carbonate is mixed with latex and then a soluble aluminum, calcium, barium or zinc salt is added to coagulate the rubber and precipitate an insoluble salt as a filler.<sup>35</sup>

#### PRODUCTS OF THE ACTION OF HEAT ON RUBBER

Mention has already been made concerning the work of Midgley, Henne and Shepard. By distilling balata and gutta-percha, it is possible to obtain products resembling linseed oil and turpentine.<sup>36</sup> Davies<sup>37</sup> found that the simple action of heat on rubber, without distillation, in the presence of magnesium or a magnesium alloy furnished a liquid miscible with oils. Further heating produced a putty-like mass; prolonged heating yielded a resin. The distillate from unvulcanized rubber, employing the same catalyst and heated in an autoclave at 240-300°C., gave rise to material which was suggested for use in paints and varnishes.<sup>38</sup> Vulcanized soft rubber or crude rubber depolymerized by melting, when mixed with molten bitumen and fibrous fillers (asbestos), has been suggested for coating pipe-lines and cables. Layers of fabric paper or pasteboard may be superimposed.<sup>39</sup>

Adhesives and insulating coatings have been obtained by Breuers<sup>40</sup> through heating rubber at 150-300°C. The rubber was first mixed with an equal weight of cyclohexane. A porous adsorbent carbon, slightly acidulated, or bleaching earth was also added in amounts of 10-50 per cent based on the weight of rubber. The product was a transparent resinous body, softening at about 50°C. and forming a thin liquid at 120-150°C. On hydrogenation it formed a solid and almost colorless resin. Butler<sup>41</sup> liquefied crude rubber by dissolving it in benzene, adding carbon tetrachloride to render the solution noninflammable and heating for 2-3 hours at 100°C. The product was utilized either alone or with added resins, oils, thinners or pyroxylin as a surfacing composition. The plastic, adhesive mass made by heating rubber at 200-350°C. followed by treatment with an inorganic acid is said to be of value in impregnating bandages.<sup>42</sup> Schidrowitz<sup>43</sup> reported that the material formed by vulcanizing latex containing ammonia (to prevent coagulation), sulphur and zinc oxide is superior in aging-properties to rubber which has been vulcanized in the dry state.

<sup>34</sup> R. S. Goodenow, U. S. P. 1,821,703, Sept. 1, 1931, one-half to G. L. Curtis; *Chem. Abs.*, 1931, 25, 6000.

<sup>35</sup> E. A. Murphy, A. Niven and D. F. Twiss, British P. 338,975, 1929, to Dunlop Rubber Co.; *Chem. Abs.*, 1931, 25, 2596. E. A. Murphy and A. Niven, British P. 373,222, 1932, to Dunlop Rubber Co., Ltd., and Anode Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 3854. E. A. Murphy and D. F. Twiss, British P. 373,262, 1932, to Dunlop Rubber Co., Ltd., and Anode Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 3853.

<sup>36</sup> H. Arias, British P. 356,203, 1929; *Chem. Abs.*, 1932, 26, 4486. Cf. the use of distillates from vulcanized and unvulcanized rubber as coating compositions, T. J. Fairley, U. S. P. 1,986,049 and 1,986,050, Jan. 1, 1935, to W. J. Hunter and M. P. Hunter; *Chem. Abs.*, 1935, 29, 1270.

<sup>37</sup> A. Davies, British P. 360,852, 1930 and 373,228, 1932; *Chem. Abs.*, 1933, 27, 1233, 3853. German P. 580,350, 1933, to Metallic Ink & Dye Co., Ltd.; *Chem. Abs.*, 1933, 27, 4956.

<sup>38</sup> A. Davies, British P. 380,934, 1930; *Chem. Abs.*, 1933, 27, 1217.

<sup>39</sup> A. Thielmann, British P. 380,893, 1932; *Brit. Chem. Abs. B*, 1932, 1041. British P. 382,147, 1932; *Chem. Abs.*, 1933, 27, 4441. See also G. Tichy and H. Klas, U. S. P. 1,991,300, Feb. 12, 1935; *Chem. Abs.*, 1935, 29, 2395.

<sup>40</sup> W. Breuers, German P. 563,506, 1931 and 576,349, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1233; 1934, 28, 683. British P. 382,755, 1931; *Brit. Chem. Abs. B*, 1933, 33. French P. 767,601, 1934; *Chem. Abs.*, 1935, 29, 626.

<sup>41</sup> H. P. Butler, British P. 274,742, 1927; *Chem. Abs.*, 1928, 22, 2291. Canadian P. 269,877, 1927; *Chem. Abs.*, 1927, 21, 3459.

<sup>42</sup> I. Giordano and O. Diena, French P. 751,348, 1933; *Chem. Abs.*, 1934, 28, 1155.

<sup>43</sup> P. Schidrowitz, *India Rubber World*, 1925, 73, 140; *Chem. Abs.*, 1926, 20, 519. U. S. P. 1,440,455, Jan. 2, 1923; *Chem. Abs.*, 1923, 17, 1351. British P. 193,451, 1923; *Chem. Abs.*, 1923, 17, 3430.

## PRODUCTS FROM THE OXIDATION OF RUBBER

The physical and chemical changes which take place in rubber on exposure to atmospheric oxidation have been frequently investigated. As early as 1861, Hofmann<sup>44</sup> observed that gutta-percha absorbed oxygen from the atmosphere, changing to a hard, brittle material. When thin films of acetone-extracted crepe rubber and balata hydrocarbons are exposed to oxygen at 85°C., rubber absorbs approximately 4 atoms of oxygen per unit of  $C_{10}H_{16}$ , whereas balata absorbs about 5 atoms.<sup>45</sup> Carbon dioxide, water, formic acid and formaldehyde can be identified in the volatile oxidation products of rubber at room temperature<sup>46</sup> whereas the solids consist of amorphous acidic substances, free from aldehyde and ketone groups but containing a small amount of peroxides.<sup>47</sup> By carrying out the oxidation with potassium permanganate in neutral or alkaline solution a series of complex, pale yellow or colorless, oxygenated, resinous products can be obtained.<sup>48</sup> These substances melt below 100-160°C. and are insoluble in acetone, alcohol or alkalies, but readily soluble in ether, benzene and ethyl acetate. Formic, acetic, oxalic and levulinic acids were also isolated. Treatment of rubber in carbon tetrachloride with chromyl chloride and decomposition of the primary product with water furnished a brown aldehydic resin. Mastication of rubber appears to entail an oxidation process.<sup>49</sup> Peroxides can be detected in the masticated product, and the oxidation reaction probably shortens the long rubber molecules.

Rubber, either in the solid state, in solution or in the form of a dispersion, when treated with an aliphatic per- acid (peracetic) or with an oxidizing mixture (acetic anhydride mixed with hydrogen peroxide) forms powdery, fibrous solids, which are more soluble in organic solvents than the original rubber and which can be added to varnishes and lacquers.<sup>50</sup> The oxidation is carried out at a temperature above 45°C. Since these materials become plastic when heated, they have been suggested as substitutes for shellac and celluloid. The polyhydroxy compounds formed by hydrolysis<sup>51</sup> may be hardened by condensation with an aldehyde. Below 80°C., acetyl peroxide and benzoyl peroxide form similar products. Rubber, for example, dissolved in chloroform, is treated with a peracetic acid mixture obtained by adding hydrogen peroxide and sulphuric acid to acetic anhydride. In this way Hopff, Ebel and Valko<sup>52</sup> produced a light yellow, tough, elastic material.

<sup>44</sup> A. W. Hofmann, *J. C. S.*, 1861, 13, 87.

<sup>45</sup> S. J. Peachey and M. Leon, *J. S. C. I.*, 1918, 37, 55T.

<sup>46</sup> A. R. Kemp, W. S. Bishop and P. A. Lasselle, *Ind. Eng. Chem.*, 1931, 23, 1444. This publication also summarizes earlier work on the subject. See also A. van Rossem and P. Dekker, (*Kautschuk*, 1929, 5, 13; *Chem. Abs.*, 1929, 23, 2598) who have studied the oxidation of vulcanized rubber. W. L. Semon, A. W. Sloane and D. Craig (*Ind. Eng. Chem.*, 1930, 22, 1001) give diagrams showing the protection of rubber by various age-resisters.

<sup>47</sup> Levulinic acid peroxide is formed in the ozonolysis of rubber or by allowing the ozonide solution to stand. It is a crystalline substance of the formula  $(C_5H_8O_4)_2$ . R. Pummerer, G. Ebermayer and K. Gerlach, *Ber.*, 1931, 64, 804; *Chem. Abs.*, 1931, 25, 4438.

<sup>48</sup> J. McG. Robertson and J. A. Mair, *J. S. C. I.*, 1927, 46, 41T.

<sup>49</sup> W. F. Busse, *Ind. Eng. Chem.*, 1932, 24, 140.

<sup>50</sup> British P. 369,716, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 651. French P. 726,961, 1931; *Chem. Abs.*, 1932, 26, 5228. Cf. the oxidation of a rubber solution with air or ozone in the presence of cobalt inoleate, H. P. Stevens and W. Young, *British P.* 417,912, 1933, to Rubber Growers' Assoc., Inc.; *Brit. Chem. Abs. B*, 1934, 1112. Oxidized rubber made in this manner (Rubbone "B,"  $C_{10}H_{16}O$ ) has been suggested as a binding material for moldings, as an ingredient for electrical insulating varnishes, paints, lacquers and adhesives. Rubbone is classified as a "drying resin" and the surface in contact with air during stoving oxidizes and "case-hardens." It may also be vulcanized with sulphur or sulphur monochloride. (See also, *Synthetic and Applied Finishes*, 1935, 6, 8; *J. S. C. I.*, 1935, 54, 221.)

<sup>51</sup> The original product is a partially acetylated hydroxy acid which, if monobasic, possesses a molecular weight of at least 1000. G. F. Bloomfield and E. H. Farmer, *J. S. C. I.*, 1934, 53, 121T. See also J. A. Mair and J. Todd, *J. C. S.*, 1932, 386. B. Kagan and N. Sukhareva, *J. Rubber Ind. (U. S. S. R.)*, 1934, 11, 46; *Chem. Abs.*, 1935, 29, 954.

<sup>52</sup> H. Hopff, F. Ebel and E. Valko, *U. S. P.* 1,983,448, Jan. 22, 1935, to I. G. Farbenind. A.-G.;

Prolonged heating of latex (containing no ammonia) with hydrogen peroxide followed by preservation with ammonia is said to furnish a good adhesive.<sup>55</sup> According to Watkins,<sup>54</sup> rubber deposited from an aqueous dispersion can be made non-tacky by treatment with a solution of an oxidizing agent, e.g., a halogen, dichromate, hypochlorite, permanganate or chromic acid. The action of benzoyl peroxide in vulcanizing rubber has been studied by Van Rossem and co-workers.<sup>55</sup> The conclusion was reached that loss of solubility in vulcanized rubber is caused by the formation of bridges through polymerization and dehydrogenation of the rubber molecules.

The sizing of paper with latex to increase its elasticity<sup>56</sup> has been found to have no special advantage since in the course of several months the latex undergoes gradual oxidation.<sup>57</sup> The addition of 5 per cent of carbon black is reported to have a beneficial effect in protecting crude rubber against the action of sunlight.<sup>58</sup>

### NITRATION OF RUBBER

The treatment of purified rubber in carbon tetrachloride solution at 0°C. with nitrogen peroxide, followed by the action of oxygen, leads both to oxidation of the rubber and to combination of a certain amount of nitrogen. However, no simple derivative has been isolated. Nitric acid yields a heterogeneous product containing an oximino group.<sup>59</sup> By the use of dilute nitric acid, Gorgas<sup>60</sup> converted rubber into two substances; one, nitrogenous and soluble in acetone; the other, non-nitrogenous and insoluble in this solvent. When urea was added to the nitric acid previous to nitration, a yellow, friable mass, free from nitrogen, was obtained. Fisher<sup>61</sup> found that rubber (500 g.) dissolved in carbon tetrachloride (6.25 l.), when agitated with 500 cc. of concentrated nitric acid for an hour, gave 833 g. of a material having the approximate formula  $(C_5H_7NO_2)_x$ . This substance was soluble in acetone and nitrobenzene, but insoluble in benzene. Its use for impregnating, coating and insulating materials was suggested. The product separated from the reaction mixture in yellow flocks and was purified by filtering and washing free from acid. It decomposed above 136°C., but, when treated with methyl sulphate, a substance stable up to 300°C. was formed. Vulcanized rubber, when submitted to the same process, yielded closely similar products.

Fischer<sup>62</sup> prepared a somewhat different substance by dissolving rubber in concentrated nitric acid. The product flocculated out on dilution with water. It was soluble in benzene and, when its solution was evaporated, remained as a film of brownish yellow varnish. With more dilute nitric acid, e.g., 1-3 parts of 50

*Chem. Abs.*, 1935, 29, 1682. German P. 556,555, 1930; *Chem. Abs.*, 1933, 27, 441. British P. 369,725, 1931; *Brit. Chem. Abs. B*, 1932, 651. French P. 41,088, 1931, addn. to 726,961, 1931; *Chem. Abs.*, 1933, 27, 1546.

<sup>55</sup> G. F. Bloomfield, E. H. Farmer and P. Schidrowitz, *Bull. Rubber Growers' Assoc.*, 1934, 16, 116; *Chem. Abs.*, 1934, 28, 4626.

<sup>54</sup> P. H. Watkins, U. S. P. 1,928,988, Oct. 3, 1933, to Naugatuck Chem. Co.; *Chem. Abs.*, 1933, 27, 6023. See also British P. 408,141, 1933, to Internat. Latex Processes, Ltd.; *Brit. Chem. Abs. B*, 1934, 512.

<sup>55</sup> A. Van Rossem, P. Dekker and R. S. Prawirodipoero, *Kautschuk*, 1931, 7, 202, 219; *Chem. Abs.*, 1932, 25, 2032.

<sup>56</sup> See F. Kaye, *India Rubber J.*, 1922, 64, 425; *Chem. Abs.*, 1922, 16, 4062.

<sup>57</sup> J. Beckoring-Vinckers, *Papier-Fabr.*, 1924, 22, 217. C. Fenchel, *ibid.*, 313; *J.S.C.I.*, 1924, 43, 976B.

<sup>58</sup> H. P. Stevens, *Bull. Rubber Growers' Assoc.*, 1924, 6, 52; *Chem. Abs.*, 1924, 18, 1066.

<sup>59</sup> Investigators have obtained a number of nitration products from rubber. C. O. Weber (*Ber.*, 1902, 35, 1947; *J.C.S.*, 1902, 82 (1), 552) obtained  $C_{10}H_{16}(NO_2)_2$  by the action of nitrogen peroxide. F. Enden, (*Ber.*, 1925, 58, 2522; *Chem. Abs.*, 1926, 20, 1238) repeating the work, could isolate only a white compound,  $C_{10}H_{16}N_2O_4$ . See also C. D. Harries, *Ber.*, 1901, 34, 2991; *J.C.S.*, 1901, 80 (1), 733.

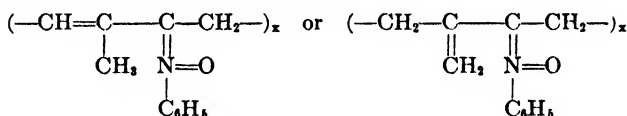
<sup>60</sup> A. Gorgas, *Ber.*, 1930, 63, 3700; *Brit. Chem. Abs. A*, 1931, 93.

<sup>61</sup> H. L. Fisher, U. S. P. 1,609,866, Dec. 7, 1926, to B. F. Goodrich Co.; *Chem. Abs.*, 1927, 21, 341.

<sup>62</sup> K. Fischer, *Gummi-Ztg.*, 1926, 40, 2387; *Chem. Abs.*, 1926, 20, 3860.

per cent acid to 100 of rubber in 400-600 parts of solvent, Oeckinghaus<sup>55</sup> has been able to produce rubber solutions characterized by having a low viscosity. Their use in spreading and dipping processes was proposed. The stickiness and slow-drying properties of a related coating (from the action of 1 part of 53 per cent nitric acid on 10 parts of rubber in 90 parts of benzene) were diminished by adding 0.5 part of antimony trichloride or phthalic acid.<sup>56</sup>

By milling rubber at 80°C. with about one-third its weight of p-nitrosodimethylaniline a sticky reaction product is obtained.<sup>55</sup> It is stated that this material, when allowed to mature for 24 hours after mastication, is useful for bonding rubber with metals or wood. It is soluble in benzene and may be employed in varnishes and lacquers. The reaction of nitrosobenzene on rubber has been studied by Bruni and Geiger.<sup>56</sup> A benzene solution of rubber and nitrosobenzene was heated on a water bath for 15 minutes, then cooled and poured into petroleum ether, yielding a yellow flocculent precipitate decomposing at 135-140°C. It analyzed for  $C_{11}H_{11}ON$  and was probably



#### HYDROGENATION OF RUBBER

Rubber is essentially an unsaturated hydrocarbon, although early investigators stated that it could not contain normal olefinic linkages since it was not very readily hydrogenated. However, evidence for the presence of double bonds in rubber was shown by Pummerer and Burkard<sup>57</sup> who succeeded in reducing a dilute solution of highly purified rubber in hexane and in methylcyclohexane by means of platinum black activated with oxygen.<sup>58</sup> This hydorrubber was similar to rubber itself in that it was highly elastic; it differed in that it was colorless, colloiddally soluble in ether and susceptible to oxidation especially when catalysts were employed.

At about the same time, Staudinger and Fritsch<sup>59</sup> succeeded in completely hydrogenating rubber by employing high temperatures and pressures (270°C. and 100 atmospheres). The hydorrubber was a colorless transparent mass without the elastic properties of ordinary rubber. Its solutions did not decolorize bromine; in sunlight a substitution product was formed.

In a similar reduction for the preparation of hydorrubber the metals of the sixth group of the periodic table are utilized as catalysts.<sup>70</sup> Lower temperatures can also be used for the hydrogenation;<sup>71</sup> for example, a 0.9 per cent solu-

<sup>55</sup> R. Oeckinghaus, U. S. P. 1,909,219, May 16, 1933, to Immalin-Werke Chem. Fabr. Eisendrath G.m.b.H.; *Brit. Chem. Abs.* B, 1934, 110.

<sup>56</sup> F. Radulesco, French P. 741,011, 1932; *Chem. Abs.*, 1933, 27, 2844. F. Radulesco, German P. 599,405, 1934, to Lack- & Farben-Fabrik Halle-Nietleben, G.m.b.H.; *Chem. Abs.*, 1934, 28, 6025.

<sup>57</sup> S. A. Brazier, E. H. Hurlston and E. V. Bratby, British P. 352,080, 1930, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 447. French P. 712,646, 1931; *Chem. Abs.*, 1932, 26, 2084. See also H. L. Fisher, Canadian P. 336,768, 1933, to Dominion Rubber Co., Ltd.; *Chem. Abs.*, 1934, 28, 2219.

<sup>58</sup> G. Bruni and E. Geiger, *Atti accad. Lincei*, 1927, (6) 5, 823; *Chem. Abs.*, 1927, 21, 4092.

<sup>59</sup> R. Pummerer and P. A. Burkard, *Ber.*, 1922, 55, 3458; *Chem. Abs.*, 1923, 17, 898.

<sup>60</sup> The platinum black was prepared by the method of R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, 1921, 54, 122. See in this connection Carleton Ellis, "Hydrogenation of Organic Substances," D. Van Nostrand Co., Inc., New York, N. Y., 1930, 88, 89, 312.

<sup>61</sup> H. Staudinger and J. Fritsch, *Helv. Chim. Acta*, 1922, 5, 785; *J.C.S.*, 1922, 122 (1), 1043. See H. Staudinger, U. S. P. 1,654,844, Jan. 3, 1928, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1928, 22, 1062.

<sup>70</sup> M. Dunkel and W. Breuers, German P. 598,000, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 5714. British P. 402,920, 1933; *Chem. Abs.*, 1934, 28, 3269. French P. 758,043, 1934; *Chem. Abs.*, 1934, 28, 3269.

<sup>71</sup> H. Staudinger and W. Feist, *Helv. Chim. Acta*, 1930, 13, 1361; *Chem. Abs.*, 1931, 25, 3519. H. Staudinger and E. O. Leupold, *Ber.*, 1934, 67, 304; *Chem. Abs.*, 1934, 28, 2944.

tion of rubber (mol.wt., 45,000 by viscosity measurements)<sup>72</sup> in methyleyclohexane was reduced, employing a platinum catalyst and carefully excluding air. With nickel as a catalyst, a temperature as low as 100°C. could be used. The molecular weight of the product was 31,000 indicating relatively little cracking. The hydro-rubber by this procedure is swelled by solvents to give highly viscous solutions and in the solid state is elastic. Its saturated character is revealed by resistance to oxidation in air and by its stability in both the solid and the liquid states.<sup>73</sup> It is largely on the characteristics of this hydorrubber that Staudinger based his belief that the physical properties of rubber are due to the long molecular chain and not to the double bonds present.<sup>74</sup> Harries and Evers<sup>75</sup> have also prepared what may be a form of hydorrubber by removing chlorine from rubber hydrochloride with zinc dust. This compound has a general semblance of gutta-percha; it is unsaturated and analysis indicates the formula,  $(C_{10}H_{18})_x$ .

By catalytic reduction Geiger<sup>76</sup> prepared hydrobutadiene rubber as an easily soluble, syrupy liquid. Further, he found that hydrogenated balata and gutta-percha are very similar to ordinary hydorrubber. In the preparation of hydro-gutta-percha equal weights of nickel and gutta-percha were treated with hydrogen at 260-300°C. The product was soluble in hydrocarbons, chloroform and carbon tetrachloride, but insoluble in acetone and alcohol. Hydrogenated methylrubber also closely resembles hydorrubber.<sup>77</sup>

Pyrolysis of Staudinger's hydorrubber at 350-400°C. yielded hydrocarbons with only one double bond. The smallest molecule was a pentene, 2-methyl-1-butene, whereas from the higher fractions were isolated hydrocarbons,  $C_{15}H_{30}$  and  $C_{50}H_{100}$ . The presence of the latter substance shows that hydorrubber must have an exceedingly high molecular weight.<sup>78</sup> In just the same way as the hydrocarbon of rubber itself is not considered as a single chemical substance, hydorrubber is thought by Staudinger to embrace a series of polymer homologues of varying complexity, depending on the procedure used in the hydrogenation.

#### USES OF HYDORRUBBER

Compared to the other types of rubber derivatives, hydorrubber has been used for relatively few commercial purposes. The material obtained by raising the temperature slowly from 100° to 280°C. during hydrogenation at 80-150 atmospheres is stated to be sufficiently strong to be employed in uniting the sheets of safety glass.<sup>79</sup> Hydorrubber has been used both alone<sup>80</sup> and with gutta-percha, balata and natural rubber<sup>81</sup> as insulation for submarine cables. Albumin was removed from the constituents of the insulation by heating with alkali and washing.<sup>82</sup>

<sup>72</sup> See Chapter 4.

<sup>73</sup> H. Staudinger, *Chem.-Ztg.*, 1934, 58, 225; *Chem. Abs.*, 1934, 28, 3615.

<sup>74</sup> This is contrary to the opinion of H. Fikentscher and H. Mark, *Kautschuk*, 1930, 6, 2; *Chem. Abs.*, 1930, 24, 3395. See Chapter 4.

<sup>75</sup> C. Harries and F. Evers, *Wiss. Veröffentl. Siemens-Konzern*, 1921, 1, 87; *Chem. Abs.*, 1922, 16, 3232.

<sup>76</sup> E. Geiger, "Über die Konstitution der Hochpolymeren," Thomsen & Hubert, Weida i Thür., 1926. *Gummi-Ztg.*, 1926, 40, 2143. See also H. Staudinger, E. Geiger, E. Huber, W. Schaal and A. Schwalbach, *Helv. Chim. Acta*, 1930, 13, 1334; *Chem. Abs.*, 1931, 25, 3518.

<sup>77</sup> H. Staudinger, M. Brunner and E. Geiger, *Helv. Chim. Acta.*, 1930, 13, 1368; *Chem. Abs.*, 1931, 25, 3518.

<sup>78</sup> H. Staudinger, *Ber.*, 1924, 57, 1202; *Chem. Abs.*, 1924, 18, 3490.

<sup>79</sup> M. Dunkel, W. Breuers and W. Wolff, U. S. P. 1,969,397, Aug. 7, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 4366. *British P.* 375,972, 1931; *Brit. Chem. Abs. B*, 1932, 888.

<sup>80</sup> *British P.* 362,049, 1930, to Felten & Guillaume Carlsberg A.-G.; *Chem. Abs.*, 1933, 27, 1237.

<sup>81</sup> K. Goes and E. Badum, U. S. P. 1,974,712, Sept. 25, 1934, to Felten & Guillaume Carlsberg A.-G.; *Chem. Abs.*, 1934, 28, 7595. *British P.* 356,041; 362,136, addn. to 362,049; 369,647, 1930; and 375,786, 1932; *Chem. Abs.*, 1933, 27, 448, 1237, 2844, 3641.

<sup>82</sup> Cf. the use of rubber itself (after removing the proteins) for the same purpose, *British P.* 307,966, 1927, to Bell Telephone Laboratories, Inc.; *Chem. Abs.*, 1930, 24, 265. F. S. Malm, *British P.* 348,567,



Plauson<sup>81</sup> proposed that the oils produced by the catalytic reduction of rubber at 130-200°C. be used in the preparation of paints and varnishes and as impregnating media for paper, cloth and leather. Hydrogenation of rubber at 270°C. while dissolved in a medium petroleum distillate furnishes a material which is stated to improve lubricating oils. Thus, 4 per cent added to a certain oil raised the viscosity from 1.95°E. at 100°C. to 2.3°E. and the viscosity index from 74 to 93.<sup>84</sup>

#### PRODUCTS FROM RUBBER AND SULPHURIC ACID OR SULPHONIC ACIDS

The transformation which takes place on treating rubber with sulphuric acid has been investigated by Kirchhof.<sup>85</sup> With carbon tetrachloride as a solvent a yellowish-white, brittle, amorphous powder was formed. It was concluded that this substance was a new hydrocarbon chemically and physically distinct from rubber. It had lost its typical rubber properties, including part of its unsaturation. The formation of an amorphous compound with formaldehyde was also observed. Fisher<sup>86</sup> has developed a number of derivatives of this type.

Cellular products were obtained by heating rubber (containing sulphur) with compounds of the general formula  $R-SO_2-X$ , e.g., a mixture of p-toluenesulphonic acid and sulphuric acid.<sup>87</sup> Shellac-like bodies may be made by heating a mixture of rubber and 1/10 of its weight of an organic sulphonic acid for 3-4 hours at 130°C. After about 1 hour, the temperature within the mass rises to 200-400°C. and bubbles of gas are given off. The artificial shellac is soluble in benzene, p-cymene, turpentine, carbon tetrachloride, tetralin, decalin and molten camphor, but insoluble in alcohol, ether, acetone, glacial acetic acid, amyl acetate, water, dilute acids and alkalis. Precipitation from solution by alcohol yields a whitish powder, softening at 90-100°C. and melting at 110-130°C. Pigments and fillers may be incorporated and hot pressed to form molded articles said to have good dielectric properties.<sup>88</sup>

The treatment of rubber with small amounts of sulphuric acid also yields tough, highly heat-plastic materials.<sup>89</sup> Five parts by weight of concentrated sulphuric acid are diluted with 1.25 parts of water and mixed with 2 parts of an inert material (titanium dioxide) to form a paste. This is then milled into 100 parts of rubber and heated in sheets at 125-130°C. for 15-20 hours. It is also possible to treat the rubber with a mixture of sulphuric acid and a sulphonic acid or a sulphonyl chloride.<sup>90</sup> Another non-tacky, thermoplastic substance was obtained by treating rubber with p-toluenesulphonic acid and sulphur.<sup>91</sup> Depending

1928, to Electrical Research Products, Inc.; *Chem. Abs.*, 1932, 26, 2803. A. R. Kemp (*J. Franklin Inst.*, 1931, 211, 37; *Chem. Abs.*, 1931, 25, 2330) has discussed the removal of nitrogenous bodies from rubber.

<sup>81</sup> H. Plauson, *British P.* 397,136, 1933; *Chem. Abs.*, 1934, 28, 931.

<sup>82</sup> French P. 761,252, 1934, to I. G. Farbenindustrie A.-G.; *Chem. Abs.*, 1934, 28, 4220.

<sup>83</sup> F. Kirchhof, *Kolloid-Z.*, 1920, 27, 311; 1922, 30, 176; *Chem. Abs.*, 1921, 15, 960; 1922, 16, 1885. *Kautschuk*, 1926, 1, 1; 1928, 4, 142; *Chem. Abs.*, 1926, 20, 1729; 1929, 23, 307. *Chem.-Ztg.*, 1923, 47, 513; *Chem. Abs.*, 1923, 17, 3112. Austrian P. 90,775, 1921, and 93,480, 1922; *Chem. Abs.*, 1929, 23, 307. See also C. Harries, "Untersuchungen über die natürlichen und künstlichen Kautschukarten." J. Springer, Berlin, 1919, 6.

<sup>84</sup> The question of priority in the discovery of these substances has been argued by Kirchhof and Fisher, F. Kirchhof, *Kautschuk*, 1928, 4, 142; 1929, 5, 48; *Chem. Abs.*, 1929, 23, 307, 2323. H. L. Fisher, *Kautschuk*, 1929, 5, 47, 65; *Chem. Abs.*, 1929, 23, 2323.

<sup>85</sup> H. L. Fisher, U. S. P. 1,786,563, Dec. 30, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1931, 25, 845.

<sup>86</sup> H. L. Fisher, U. S. P. 1,668,235, May 1, 1928, to B. F. Goodrich Co.; *Chem. Abs.*, 1928, 22, 2291. *Plastics*, 1928, 613. See also British P. 249,172, 1934; *Chem. Abs.*, 1927, 21, 1031.

<sup>87</sup> H. L. Fisher, U. S. P. 1,668,236, May 1, 1928, to B. F. Goodrich Co.; *Brit. Chem. Abs. B.*, 1928, 404. Cf. the use of sulphuric acid to give rubber articles a hard flexible surface, British P. 417,563, 1934, to Internat. Latex Processes, Ltd.; *Chem. Abs.*, 1935, 29, 1683.

<sup>88</sup> H. L. Fisher, U. S. P. 1,668,237, May 1, 1928, to B. F. Goodrich Co.; *Brit. Chem. Abs. B.*, 1928, 494.

<sup>89</sup> H. L. Fisher, U. S. P. 1,731,483, Oct. 15, 1929, to B. F. Goodrich Company; *Chem. Abs.*, 1930, 24, 265.

upon the proportion of reagents used and the temperature and duration of heating, resilient, elastic products, resembling soft vulcanized rubber, tough, thermoplastic, balata-like substances or a hard, friable, shellac-like material resulted.

The products formed by the action of organic sulphonic acids on rubber have been recommended for the insulation of marine cables.<sup>92</sup> The reaction is carried out in the following manner: 3 parts of pine tar and 7 of concentrated sulphuric acid are worked into 100 of crude rubber and the mixture heated in an oven until a marked rise in temperature is noted (200-250°C.). This requires about 75 minutes at 130°C., heating being then continued for 2 hours, until a maximum temperature is noted. After cooling, the product is masticated in a warm mill and washed free from impurities. In order to soften the mass, various materials are added, e.g., turpentine, phenol, naphthalene, paraffin, oleic acid, furfural, stearic acid and phthalic anhydride.<sup>93</sup> A similar moldable body, which may be used in the production of insulation, radio parts and phonograph records, is produced by the action of sulphonyl chlorides and sulphuric acid, either together or separately, upon a mixture of crude rubber, vulcanized rubber scrap and pine tar.<sup>94</sup> Another thermoplastic material has been prepared by Winkelmann<sup>95</sup> through the use of a multivalent metal and an organic sulphonic acid.

The plasticity of the products from rubber and substituted sulphonic acids has also been modified by incorporating a wax or an oil of a low water-absorption capacity.<sup>96</sup> Thus, a composition for making sound records is prepared by mixing 300 parts of the hard material (produced from rubber, sulphuric acid and p-toluenesulphonic acid) with 100-250 parts of infusorial earth, 100-300 of ferric oxide, 10-50 of gas black, 10-50 of cotton flock and 10-50 of paraffin, stearic acid or palm oil.<sup>97</sup>

Incorporation of 10 per cent or more of diethyl sulphate with rubber, followed by heating for 8 hours at 125-140°C., yields a tough, stable, thermoplastic material dark in color.<sup>98</sup> It dissolves in the well-known rubber solvents including benzene, carbon tetrachloride and carbon disulphide, but is insoluble in alcohol, ether, water and dilute acids or alkalis.

A rubberized paint is obtained upon dissolving the product formed by heating rubber with phenolsulphonic acid for 6 hours at 140°C. Pigments, fillers, flowing-agents and preservatives or antioxidants are added.<sup>99</sup> Gray<sup>100</sup> reports that tests on this paint indicate resistance to chemical action and to penetration by water and that it is satisfactorily adhesive and elastic. The rubber isomer can also be employed in a nitrocellulose lacquer providing the solvent in the latter contains

<sup>92</sup> W. C. Geer, U. S. P. 1,731,484, 1,731,485 and 1,731,487, Oct. 15, 1929, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 264. See also A. R. Kemp, U. S. P. 1,874,307, Aug. 30, 1932, to Bell Telephone Laboratories, Inc.; *Chem. Abs.*, 1932, 26, 6037. British P. 348,192, 1930, to Electrical Research Products, Inc.; *Brit. Chem. Abs. B*, 1931, 726.

<sup>93</sup> W. C. Geer and H. A. Winkelmann, U. S. P. 1,705,757, Mar. 19, 1929, to B. F. Goodrich Co.; *Chem. Abs.*, 1929, 23, 2324.

<sup>94</sup> H. A. Winkelmann, U. S. P. 1,716,474, June 11, 1929, to B. F. Goodrich Co.; *Chem. Abs.*, 1929, 23, 3828. See also H. Gray, U. S. P. 1,748,926, Feb. 4, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 1764. British P. 260,637, 1925; *Brit. Chem. Abs. B*, 1927, 610.

<sup>95</sup> H. A. Winkelmann, U. S. P. 1,890,924, Dec. 13, 1932; to B. F. Goodrich Co.; *Brit. Chem. Abs. B*, 1933, 801.

<sup>96</sup> W. C. Geer and H. L. Fisher, U. S. P. 1,731,849, Oct. 15, 1929, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 264.

<sup>97</sup> H. L. Fisher and W. C. Geer, U. S. P. 1,731,483, Oct. 15, 1929, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 264.

<sup>98</sup> H. L. Fisher and H. A. Winkelmann, U. S. P. 1,782,140, Nov. 18, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1931, 25, 437.

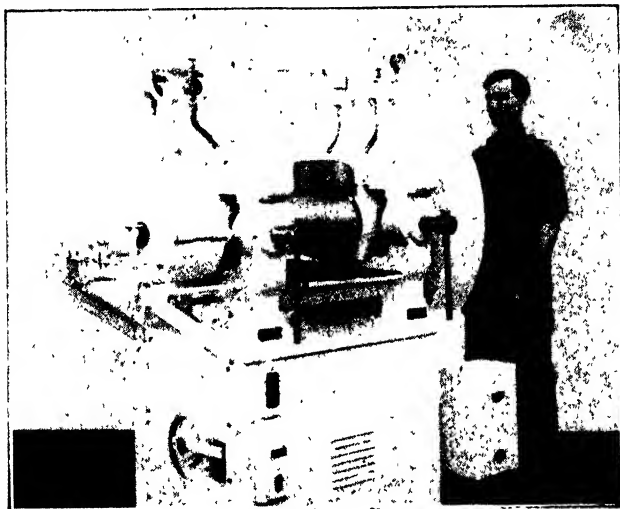
<sup>99</sup> W. C. Geer, U. S. P. 1,744,881, Jan. 28, 1930, to B. F. Goodrich Co.; *Brit. Chem. Abs. B*, 1930, 997. The Goodrich Co. manufactures a series of "Acidseal" paints which contain rubber and possess a wide range of properties. R. H. Harrington (U. S. P. 1,983,367, Dec. 4, 1934, to General Elec. Co.; *Chem. Abs.*, 1935, 29, 527. British P. 418,348, 1934, to Brit. Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1935, 30) has employed chromium sesquioxide with a rubber isomer (from rubber and phenol-sulphonic acid) in electrical insulating coatings.

<sup>100</sup> H. Gray, *Ind. Eng. Chem.*, 1928, 20, 156.

toluene.<sup>101</sup> A further application of such transformation products is as undercoatings for cellulose esters.<sup>102</sup>

A laminated stock for battery cases has been formed by superimposing sheets of thermoplastic material and heat-curable natural rubber followed by vulcanizing together.<sup>103</sup> A typical formula for the synthetic layer consists of heat plastic from rubber and p-phenolsulphonic acid (86 parts), aldol- $\alpha$ -naphthylamine (3 parts), benzidine (1 part) and tung oil (10 parts).

Fisher<sup>104</sup> applied the name "Thermoprene" to the products made by heating raw rubber with the above-mentioned sulphonic compounds. These materials differ from vulcanized rubber in having the same empirical composition,  $(C_5H_8)_x$ , as the original rubber, i.e., they contain no combined sulphur. Their properties



Courtesy Parrel-Birmingham Co., Inc.

FIG. 141.—Laboratory Mill for Rubber and Other Plastics.

vary with the agent used and the time and temperature of heating, but in general resemble either gutta-percha, balata or shellac.<sup>105</sup> All three types combine with sulphur to form hard products which are no longer thermoplastic and are insoluble in organic solvents. The purified chief component of the shellac-like material could not be hydrogenated catalytically but was nitrated, forming a compound,  $C_6H_7NO_2$ .

A related thermoplastic conversion-product of rubber is described by Robinson.<sup>106</sup> Rubber is liquefied by mastication and by heating in an atmosphere of carbon dioxide at 250-270°C. The liquid is then subjected to treatment with sulphuric acid or a sulphonic acid at 150°C., yielding a rather hard black mass

<sup>101</sup> C. H. Siever, U. S. P. 1,785,387, Dec. 16, 1930; *Brit. Chem. Abs.* B, 1931, 818.

<sup>102</sup> C. Bogin, U. S. P. 1,965,627, July 10, 1934, to Commercial Solvents Corp.; *Chem. Abs.*, 1934, 28, 5692. Cf. the use of depolymerized rubber as a cushioning-stratum in photographic film, S. E. Sheppard and S. S. Sweet, U. S. P. 1,623,500, Apr. 5, 1927, to Eastman Kodak Co.; *Chem. Abs.*, 1927, 21, 1599.

<sup>103</sup> W. C. Geer, U. S. P. 1,617,707, Feb. 15, 1927, to B. F. Goodrich Co.; *Chem. Abs.*, 1927, 21, 1377.

<sup>104</sup> H. L. Fisher, *Ind. Eng. Chem.*, 1927, 19, 1325. H. L. Fisher and E. M. McCollm, *ibid.*, 1328. See also F. Kirchhof, *Kautschuk*, 1928, 4, 143; *Brit. Chem. Abs.* B, 1928, 763.

<sup>105</sup> These three general types are designated as Thermoprene-GP, Thermoprene-HB and Thermoprene-SL, respectively.

<sup>106</sup> E. B. Robinson, British P. 339,398, 1929 to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs.* B, 1931, 363. French P. 702,809, 1930; *Chem. Abs.*, 1931, 25, 4370. German P. 578,356, 1933; *Chem. Abs.*, 1933, 27, 4440.

(softening point 100°C.). By mixing together equal parts of this material and crepe rubber an adhesive for uniting rubber to fabrics has been obtained.<sup>107</sup> Another adhesive, suggested for uniting rubber to metal,<sup>108</sup> is produced by creaming latex with a weak organic acid, adding a strong acid such as sulphuric acid, evaporating the volatile material and baking at 150°C. Geer<sup>109</sup> has also employed the balata- or shellac-like isomers as adhesives, using benzene as a solvent and tung oil or castor oil as softeners. A very similar material has been produced through the action of the acid on rubber mixed with balata and gutta-percha resins.<sup>110</sup> For uniting rubber to metals, glass or hard rubber, an adhesive obtained by the action of formaldehyde on rubber in the presence of hydrochloric, phosphoric or sulphuric acid has been proposed.<sup>111</sup>

Rubber and the polymerization products of butadiene hydrocarbons have been dissolved in indifferent solvents and treated with carboxylic anhydrides, e.g., acetic anhydride, in presence of such acids as acetylsulphuric acid or sulphobenzoic acid. This transformed the rubber into a material intended for waterproofing and impregnating textiles.<sup>112</sup> Rubber or polymerized butadiene may also be sulphonated with chlorosulphonic acid in an organic diluent, e.g., ether, and used either in solution or emulsion form as tanning agents or as sizing- and dressing-assistants in the textile industry.<sup>113</sup> Oenslager's method of increasing the durability of rubber may be mentioned here.<sup>114</sup> Rubber which has been applied to articles of various shapes is treated with sulphur dioxide and oxygen under pressure.

#### ACTION OF NON-METALLIC HALIDES ON RUBBER

A further group of materials is obtainable by the action of metallic and non-metallic halides on rubber. Thus, aluminum chloride in conjunction with phthalyl chloride reacts with benzene solutions of the hydrocarbon below 100°C. to yield bodies which are said to have good wearing qualities after vulcanization.<sup>115</sup> Kirchhof<sup>116</sup> has studied the analogous action of benzoyl chloride on rubber in carbon tetrachloride solution using aluminum chloride as catalyst. This procedure yields a gray-white, spongy mass, which, after evaporation and extraction, remains as a brittle, amorphous body. The actual nature of the product varies greatly with the conditions of preparation. These benzylidene rubbers are pulverized with great ease and are thermoplastic above 100°C.

<sup>107</sup> R. B. F. Clarke, British P. 392,966, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 5908.

<sup>108</sup> R. B. F. Clarke, E. B. Robinson and A. Shepherdson, British P. 357,238, 1930, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1931, 1109.

<sup>109</sup> W. C. Geer, British P. 247,136, 1925; *Chem. Abs.*, 1927, 21, 631. See also French P. 696,754, 1930, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 2866. For a study of Thermoprene cements, see B. Fabritzjev, G. Buiko and E. Pakhomova, *Kozhevnikovo-Obuvnaya Prom.*, 1934, 13, 522; *Chem. Abs.*, 1935, 29, 2391.

<sup>110</sup> D. F. Twiss, A. A. Round and E. A. Murphy, British P. 343,531, 1929, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1932, 26, 2892. D. F. Twiss, F. A. Jones and J. H. Anderson, British P. 395,430, 1932, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs. B*, 1933, 27, 3639. French P. 746,956, 1933; *Chem. Abs.*, 1933, 27, 4891. German P. 575,226, 1933; *Chem. Abs.*, 1933, 27, 3639.

<sup>111</sup> D. F. Twiss and F. A. Jones, British P. 348,303, 1930, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 447. Cf. the preparation of an adhesive from resins extracted from balata or gutta-percha, D. F. Twiss and F. A. Jones, British P. 371,339, 1931, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs. B*, 1932, 689. German P. 577,802, 1933; *Chem. Abs.*, 1934, 28, 687.

<sup>112</sup> H. Hopff, F. Ebel and K. Wolf, French P. 723,838, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4981. German P. 549,759, 1930; *Chem. Abs.*, 1933, 27, 555.

<sup>113</sup> E. Konrad and H. Kleiner, German P. 582,565, 585,622 and 585,623, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 686, 1572. See also British P. 386,752, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 261. German P. 572,930, 1933; *Chem. Abs.*, 1933, 27, 4440. French P. 740,409, 1932; *Chem. Abs.*, 1933, 27, 2314.

<sup>114</sup> G. Oenslager, U. S. P. 1,925,879, Sept. 5, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 5578.

<sup>115</sup> H. Mark and H. Hopff, German P. 555,845, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 2901. French P. 704,757, 1930; *Chem. Abs.*, 1931, 25, 4740. British P. 347,108, 1930; *Chem. Abs.*, 1933, 27, 448. A vulcanized composition containing both rubber and a rubber isomer has been employed as a binder in abrasive wheels. R. C. Benner, British P. 377,291, 1931, to Carborundum Co., Ltd.; *Brit. Chem. Abs. B*, 1932, 667. Belting and footwear have also been prepared from vulcanized rubber isomers. B. S. Taylor, U. S. P. 1,886,759, Nov. 8, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 1546.

<sup>116</sup> F. Kirchhof, *Kautschuk*, 1931, 7, 125; *Chem. Abs.*, 1931, 25, 6015.

Rubber, in the presence of a solvent if desired, may also be treated with a phosphoryl halide at 15-40°C. The diluent is distilled off, and excess of the phosphorus compound is washed out with dilute ammonia leaving a material which softens at 100-110°C.<sup>117</sup> Plastic masses have been obtained also by treating rubber with a mixture of phosphorus trichloride and oxychloride<sup>118</sup> and with phosphorus compounds containing more oxygen than the oxyhalides.<sup>119</sup>

The halides of sulphur likewise have been used in rubber fabrication.<sup>120</sup> Twiss and Jones<sup>121</sup> and also Taylor<sup>122</sup> employed such substances as thionyl chloride, sulphur chloride and phosphorus pentachloride and pentasulphide in the surface-treatment of rubber articles to make them harder and more oil-resistant. Films and threads may be made by treating the polymerization products of hydrocarbons of the butadiene series with sulphurizing agents (e.g., sulphur dichloride) until the high-elasticity characteristic of rubber disappears.<sup>123</sup> This process may be applied also to polymers made from natural rubber, the product in either case being improved by incorporation of paraffin hydrocarbons of high molecular weight, cycloparaffins or waxes.<sup>124</sup> Resin-like bodies are obtained by treating a solution of rubber with sulphur chloride, sulphur dichloride or sulphuryl chloride and after removal of the solvent working up the material by the application of heat and pressure.<sup>125</sup> Gouillardon<sup>126</sup> has employed a solution of sulphur chloride in carbon tetrachloride to fasten rubber surfaces together. Rubber derivatives intended to find application in the manufacture of dyestuffs and pharmaceuticals have been obtained by the action of aryl or alkyl sulphur halides on rubber in an indifferent solvent. For example, a solution of p-nitrophenyl-sulphur chloride in carbon tetrachloride gives with rubber dissolved in the same solvent a bright yellow, additive product sintering at about 135°C.<sup>127</sup>

#### ACTION OF METALLIC SALTS ON RUBBER

Bruson<sup>128</sup> treated solutions of rubber with various metallic halides. Colored addition products were formed first, that from stannic chloride having the formula,  $(C_2H_5)_{10}SnCl_4$ . Removal of the metal halide with alcohol in an inert atmosphere yielded a benzene-soluble material which, when heated, became brittle and resembled shellac in appearance. Admission of air during the treatment with alcohol resulted in powdery insoluble oxides of the rubber polymers. In exhibiting this series of reactions, rubber resembles other unsaturated hydrocarbons, e.g., isoprene, cyclopentadiene and indene. To render surfaces of rubber articles hard and polishable, Geer<sup>129</sup> treated them with solutions of stannic chloride in ethylene dichloride

<sup>117</sup> E. Walz, U. S. P. 1,987,171, Jan. 8, 1935, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1544. British P. 332,762, 1929; *Brit. Chem. Abs. B.*, 1930, 993.

<sup>118</sup> E. Walz, German P. 535,687, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1155.

<sup>119</sup> French P. 752,502, 1933, to Walpamur Co., Ltd.; *Chem. Abs.*, 1934, 28, 1232.

<sup>120</sup> L. Hull (British P. 67, 1863) proposed to restore the elasticity of milled rubber with a solution of sulphur chloride in light petroleum oil.

<sup>121</sup> D. F. Twiss and F. A. Jones, British P. 410,436, 1933, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs. B.*, 1934, 639.

<sup>122</sup> B. S. Taylor, U. S. P. 1,886,759, Nov. 8, 1932, to B. F. Goodrich Co.; *Brit. Chem. Abs. B.*, 1933, 722.

<sup>123</sup> French P. 676,658, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 3135.

<sup>124</sup> French P. 39,424, 1930, addn. to 676,658, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2347.

<sup>125</sup> German P. 590,605, 1934, to Artifex chem. Fabrik G.m.b.H.; *Chem. Abs.*, 1934, 28, 3270.

<sup>126</sup> S. Gouillardon, French P. 384,061, 1908. See also French P. 336,654, 1903, to Soc. anon. des pneumatiques cuir "Samson."

<sup>127</sup> British P. 313,919, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1930, 373.

<sup>128</sup> H. A. Bruson, U. S. P. 1,846,347, Feb. 23, 1932, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1932, 26, 2621. British P. 285,071, 1927; *Brit. Chem. Abs. B.*, 1929, 367. Canadian P. 299,963, 1930; *Chem. Abs.*, 1930, 24, 3135. See also H. A. Endres (Canadian P. 239,070, 1934, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1934, 28, 2553. French P. 753,027, 1933; *Chem. Abs.*, 1934, 28, 917) for the preparation of coating compositions. H. A. Bruson, L. B. Sevrill and W. C. Calvert, *Ind. Eng. Chem.*, 1927, 19, 1033.

<sup>129</sup> W. C. Geer, U. S. P. 1,948,292, Feb. 20, 1934; *Chem. Abs.*, 1934, 28, 2962. J. W. Baymiller, British P. 409,772, 1934, to W. C. Geer, *Chem. Abs.*, 1934, 28, 6348.

or ethyl acetate. A similar procedure has been employed to stabilize the color of rubber objects.<sup>120</sup>

When 10 per cent by weight of chlorostannic acid,  $\text{H}_2\text{SnCl}_6 \cdot 2\text{H}_2\text{O}$ , was milled into rubber and heated for 2-5 hours at 130-150°C., a tough, balata-like material resulted.<sup>121</sup> Long heating or excessive temperature formed a hard, ebony-like substance.<sup>122</sup> Both products are light colored and are soluble in benzene and petroleum hydrocarbons, but treatment with chlorine water increases their resistance to these solvents.<sup>123</sup> These bodies were proposed as plastics<sup>124</sup> and as binders for laminated material. A related composition was made by treating a benzene solution of rubber with chlorostannic acid at 65-80°C. After the viscosity had reached the desired value, the reagent was decomposed with water and the solvent distilled off.<sup>125</sup> An examination of the higher fatty acid salts of copper, manganese, iron and mercury, which disperse well with rubber, showed that all of these compounds are deleterious to the aging of vulcanized rubber.<sup>126</sup> On the other hand, Stine and Booge<sup>127</sup> have recommended the use of a rubber solution containing cobalt linoleate as a coating composition. After evaporation of the solvent, the cobalt salt brought about oxidation to a hard, durable, waterproof film.<sup>128</sup> A further reaction of metallic compounds is the reversible vulcanization by Grignard reagents and zinc alkyls observed by Midgley, Henne and Shepard.<sup>129</sup>

The halides of the amphoteric metals are reported as especially adapted to the preparation of thermoplastic materials.<sup>130</sup> Some of the halides of aluminum, chromium, iron, antimony, bismuth, manganese, tin, zinc, vanadium and zirconium are reported to be satisfactory for this purpose. The production of a thermoplastic body using ferric chloride, for example, is carried out as follows: 10 parts by weight of ferric chloride are milled into 100 parts of crude rubber, and the mass is subjected to dry heat at 160°C. for 15 hours. A strongly exothermic reaction takes place between the salt and the rubber, the temperature rising to 200-250°C. The product is a hard, brittle, heat-plastic material with a relatively low softening point. It is black in color, breaks with a conchoidal fracture and chemically is more saturated than the rubber from which it was prepared. The products from zinc bromide and zinc chloride are brown and somewhat transparent; those from antimony chloride or bromide are yellow; and those from bismuth chloride, a light gray. There is a tendency for the activity of the halide to increase with increasing atomic weight of the halogen atom, which may explain the inactivity of the fluorides in bringing about this type of reaction.

<sup>120</sup> W. C. Geer, British P. 410,171, 1932; *Brit. Chem. Abs.* B, 1934, 639

<sup>121</sup> H. A. Bruson, Canadian P. 299,963, 1930, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1930, 24, 3135.

<sup>122</sup> These resins have been placed on the market by the Goodyear Tire & Rubber Co. as molding materials ("Phoform") and as alkali-resistant coatings ("Pholite"). See H. R. Thies, *Paint, Oil and Chem. Rev.*, 1935, 98 (8), 22. H. A. Endres, *ibid.*, 1934, 97 (8), 9. See also H. Chase, *Synthetic and Appl. Finishes*, 1935, 6, 12.

<sup>123</sup> H. R. Thies and A. M. Clifford, *Ind. Eng. Chem.*, 1934, 26, 123.

<sup>124</sup> A proposed adhesive is formed by the action of fluoboric acid on rubber. H. A. Bruson, U. S. P. 1,853,334, Apr. 12, 1932, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1932, 26, 3407.

<sup>125</sup> French P. 768,262, 1934, to Wingfoot Corp.; *Chem. Abs.*, 1935, 29, 522.

<sup>126</sup> B. S. Taylor and W. N. Jones, *Ind. Eng. Chem.*, 1928, 20, 132. See also H. C. Jones and H. A. Depew, *Ind. Eng. Chem.*, 1931, 23, 1467. The retarding action of tetramethylthiuram monosulphide is due to the formation of an insoluble compound.

<sup>127</sup> C. M. A. Stine and J. E. Booge, U. S. P. 1,700,779, Feb. 5, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1929, 23, 1528. See also C. M. A. Stine and C. Coolidge, U. S. P. 1,721,930 and 1,721,931, July 23, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1929, 23, 4553. Too rapid oxidation can be prevented by the addition of phenolic compounds. C. M. A. Stine, C. Coolidge and E. B. Middleton, U. S. P. 1,700,778, Feb. 5, 1929, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1929, 23, 1516. Cellulose esters may also be included. C. M. A. Stine and C. Coolidge, U. S. P. 1,723,632, Aug. 6, 1929, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs.* B, 1929, 826.

<sup>128</sup> The resin extracted from crude balata or gutta-percha has been neutralized and then hardened by blowing with air in the presence of manganese resinate. A. B. Craven, British P. 278,923, 1927, to the Yorkshire Dyeware & Chemical Co., Ltd.; *Chem. Abs.*, 1928, 22, 2850.

<sup>129</sup> T. Midgley, Jr., A. L. Henne and A. F. Shepard, *J.A.C.S.*, 1934, 56, 1156.

<sup>130</sup> W. N. Jones and E. A. Winkelmann, U. S. P. 1,751,817, Mar. 26, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 2659. German P. 539,106, 1926; *Chem. Abs.*, 1932, 26, 1156. See also J. Scheiber, P. 530,136, 1923; *Chem. Abs.*, 1933, 27, 4945.

Gray<sup>141</sup> reports that turpentine when heated with stannous sulphate yields a material useful for bonding metal to rubber. The same investigator also used a mixture of a heat-plastic rubber isomer with a lead salt of a higher fatty acid, e.g., lead oleate, as a rubber cement.<sup>142</sup> Sebrell<sup>143</sup> developed a related method for securing fibrous or porous materials to metals or to each other. For example, 1346 g. of a cement containing 20.8 per cent of rubber were mixed with 30 cc. of a solution consisting of equal parts of benzene and thin pine oil. To this were added 4.9 cc. of anhydrous stannic chloride in 1200 cc. of benzene. The solution was heated at 80°C. for 2 hours and then cooled. The surfaces to be joined are coated with the liquid and pressed together at 80-100°C. for 10-30 minutes. A solution of sulphur and zinc butyl xanthate also has been proposed for joining rubber surfaces.<sup>144</sup>

#### PHENOLIC SUBSTANCES AND RUBBER

Plastic materials for electrical insulation may be obtained from rubber and formaldehyde, or rubber, formaldehyde and phenol. Such bodies have certain properties of both hard rubber and phenol resin. McGavack<sup>145</sup> stated that some chemical combination occurred between the rubber, phenol and aldehyde, i.e., the result was not merely a mixture of phenol resin and rubber. The following example illustrates the procedure: 15 kg. of pale crepe rubber are dissolved in 300 kg. of carbon tetrachloride, 25 kg. of sulphuric acid (sp.gr. 1.84) being stirred in to serve as a condensing agent. Forty kg. of 40 per cent formaldehyde solution are added, and the mixture is refluxed for 2-3 hours at 100°C. The resulting grayish-white product, containing free acid, formaldehyde and carbon tetrachloride, is treated with 100 kg. of water, and the carbon tetrachloride is distilled off, 90 per cent being recovered. The mass is washed with running water until free from acid, dried and milled on a cold mill. Then it is heated at 95°C. until dry. The brownish black powder, which is obtained finally, can be molded at 140-160°C. under a pressure of 3000-4000 pounds per square inch. It has a specific gravity of 1.05 at 18°C., softens at 130°C., has a transverse tensile strength of about 400 pounds per square inch and is almost insoluble in all acids, bases and organic solvents. The molded articles will take a high polish and may be machined, turned, sawed or drilled. If, in the above procedure, the formaldehyde is replaced by 15 kg. of butyraldehyde or 15 kg. of furfural, the products have similar properties but somewhat lower softening points.

A further variation is the use of latex, 100 kg. being treated with 650 kg. of carbon tetrachloride and the mixture shaken until a smooth emulsion results. Then, 30 kg. of phenol and 80 kg. of 40 per cent formaldehyde are added. After mixing, 40 kg. of concentrated sulphuric acid are run in and the mixture refluxed for 2 or 3 hours at 100°C., washed, dried and molded. Vulcanized rubber may also be utilized as a raw material<sup>146</sup> in which case it is first chlorinated. For example, 100 g. of ground vulcanized rubber, containing 1-5 per cent of combined sulphur, are dispersed or swollen in a container with 1 kg. of benzol. Chlorine is then introduced at the rate of about 10 cc. per minute per g. of rubber, until the rubber

<sup>141</sup> H. Gray, U. S. P. 1,697,275, Jan. 1, 1929, to B. F. Goodrich Co.; *Chem. Abs.*, 1929, 23, 1309.

<sup>142</sup> H. Gray, U. S. P. 1,782,036, Nov. 18, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1931, 25, 437. See also H. Gray, U. S. P. 1,801,667, Apr. 21, 1931, to B. F. Goodrich Co.; *Brit. Chem. Abs. B*, 1931, 1148.

<sup>143</sup> L. B. Sebrell, British P. 310,461, 1929, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1930, 24, 752.

<sup>144</sup> F. S. Malm, British P. 353,437, 1929, to Electrical Research Products, Inc.; *Chem. Abs.*, 1933, 27, 448.

<sup>145</sup> J. McGavack, U. S. P. 1,640,363, Aug. 30, 1927, to Revere Rubber Co.; *Chem. Abs.*, 1927, 21, 3490. See *Plastics*, 1927, 661.

<sup>146</sup> J. McGavack, U. S. P. 1,640,364, Aug. 30, 1927, to Revere Rubber Co.; *Chem. Abs.*, 1927, 21, 3490. See also *Plastics*, 1927, 679.

molecule contains 56-58 per cent of chlorine. One hundred fifty g. of phenol and 150 g. of 40 per cent aqueous formaldehyde solution are added and the mixture boiled under reflux for 2-3 hours. The brownish emulsion is then steam distilled to remove excess of chlorine and solvent; and the solid product, containing 35 per cent of combined chlorine, is washed, dried and molded. Other phenolic substances, as well as higher aldehydes, may be used in the above process.<sup>147</sup>

Fisher<sup>148</sup> has suggested the production of a plastic material formed from rubber by the action of trichloroacetic acid. The following is an example of the general procedure: 100 parts by weight of a 5 per cent solution of rubber in benzene are mixed with 6 parts of trichloroacetic acid, and the mixture heated under reflux for 2 days. Then the solvent is distilled off and the solid residue is washed. The mass is homogenized by mastication or by redissolving in an organic solvent. In one modification of this method a phenol is employed. For example, 100 parts by weight of 5 per cent rubber solution, 10 parts of phenol and 6 parts of trichloroacetic acid are mixed and heated on a steam bath, the solid being recovered as before. These materials are tough and somewhat friable and are heat-plastic at ordinary molding temperatures. They are soluble in the common rubber solvents (e.g., benzene, gasoline and turpentine), but practically insoluble in alcohol, ether, acetone, aniline, water and dilute acids or alkalies. Rubber may also be made to yield thermoplastic materials by heating with a phenol and a third substance.<sup>149</sup> The latter may be one of a large number of compounds, including chlorinated rubber, rubber hydrochloride, aniline hydrochloride, trichloroaniline hydrochloride, mercuric chloride, stannic chloride, aluminum sulphate, naphthalene tetrachloride, m-nitraniline hydrochloride or pinene hydrochloride.

A further group of reagents suggested for converting rubber-phenol mixtures into moldable bodies includes sulphonyl chlorides and dilute sulphuric acid.<sup>150</sup> Vulcanized rubber when similarly heated at 100°C. with benzene, phenol and hydrochloric or hydrobromic acid yields an adhesive.<sup>151</sup>

#### MISCELLANEOUS PRODUCTS FROM RUBBER

Prolonged contact with thioglycolic acid converts rubber into a glassy resinous material of the formula,  $(C_6H_5-S-CH_2-CO_2H)_n$ .<sup>152</sup> Allowing polymerized butadiene to stand in dilute alkali is said to prevent resinification.<sup>153</sup> Cathode rays have been observed to transform rubber in a manner similar to vulcanization.<sup>154</sup> Rubber-impregnated fabrics (e.g., conveyor belts) have been rendered acid-resistant by alternate coatings of a thermoplastic rubber isomer and of an elastic mixture containing a natural gum-resin and a drying oil.<sup>155</sup>

<sup>147</sup> R. P. Courtney (British P. 356,769, 1930, to Bakelite Corp.; *Brit. Chem. Abs.* B, 1931, 1062) prepared a cement by incorporating rubber in an oil-modified phenol resin.

<sup>148</sup> H. L. Fisher, U. S. P. 1,642,018, Sept. 13, 1927, to B. F. Goodrich Co.; *Brit. Chem. Abs.* B, 1927, 917. See also *Plastics*, 1928, 135.

<sup>149</sup> H. L. Fisher, U. S. P. 1,852,294 and 1,852,295, Apr. 5, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1932, 26, 3142. British P. 282,778, 1926; *Chem. Abs.*, 1928, 22, 4007. See also French P. 646,414, 1927; *Chem. Abs.*, 1929, 23, 2324. German P. 538,941, 1927; *Chem. Abs.*, 1932, 26, 2246. Canadian P. 284,980 and 284,981, 1928; *Chem. Abs.*, 1929, 23, 1013.

<sup>150</sup> H. L. Fisher, U. S. P. 1,852,345 and 1,852,346, Apr. 5, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1932, 26, 3142. French P. 648,759, 1927; *Chem. Abs.*, 1929, 23, 3375. British P. 307,184, 1927; *Brit. Chem. Abs.* B, 1929, 367. German P. 571,183, 1927; *Chem. Abs.*, 1933, 27, 2844.

<sup>151</sup> H. L. Fisher, U. S. P. 1,852,294, Apr. 5, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1932, 26, 3142.

<sup>152</sup> B. Holmberg, *Ber.*, 1932, 65, 1349; *Brit. Chem. Abs.* A, 1932, 1139.

<sup>153</sup> British P. 29,213, 1911, to Farbenfabr. vorm. F. Bayer & Co.; *Chem. Abs.*, 1913, 7, 426. German P. 257,818, 1911; *Chem. Abs.*, 1913, 7, 2695. German P. 264,820, 1911; *Chem. Abs.*, 1914, 8, 1855.

<sup>154</sup> E. B. Newton, U. S. P. 1,906,402, May 2, 1933, to B. F. Goodrich Co.; *Brit. Chem. Abs.* B, 1934, 110.

<sup>155</sup> R. S. Taylor and B. M. Costello, U. S. P. 1,906,434, May 2, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 3639.



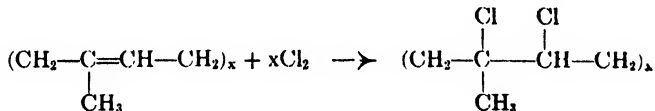
## Chapter 55

### Resins from Rubber II. Halogenated Rubber

The halogens react directly with rubber, gutta-percha or balata to form an interesting series of compounds possessing properties intermediate between those of rubber and the brittle natural resins. The extent of the halogenation in the case of chlorine can be varied to produce compounds containing as much as 70 per cent of halogen. This highly chlorinated rubber together with derivatives containing less chlorine furnish a graduated series of products with elastic properties varying from that of the original rubber to one of a tough, leather-like resin. The halogenated bodies are chemically inactive and are more soluble than the original stock in carbon tetrachloride, carbon bisulphide, chloroform, acetone and ether from which they may be precipitated by alcohol. The solutions possess much lower viscosity than those of the original material and find use as bases of coating compounds and lacquers. Although chlorine is ordinarily employed, both bromine and iodine react with rubber. The color of the halogenated compounds varies from a pale-yellow to pure white. They do not burn, and, when heated soften without melting; decomposition occurs before the true melting point is reached. They possess electrical insulating properties. When mixed with various fillers they form compositions which can be hot-molded; the final products are more tough than brittle, and can be worked into masses resembling leather. Moreover somewhat similar compounds are formed by the action of the hydrogen halides on rubber and related materials.

#### MECHANISM OF HALOGENATION

On the basis of the structure of the rubber molecule,<sup>1</sup> halogen could add directly to the unsaturated bond. Chlorine, for example, should furnish a chloro hydrocarbon containing 51 per cent of chlorine.

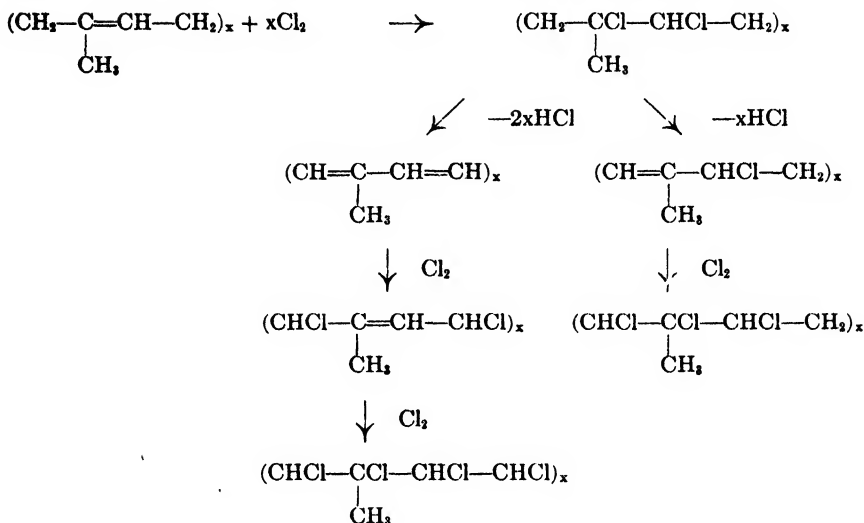


In practice, however, both addition and substitution occur inasmuch as hydrogen chloride is evolved. Moreover the compound, which is isolated, contains more halogen than the above equation would indicate.

Numerous explanations have been offered to account for this phenomenon. Kirchhof<sup>2</sup> suggested that the initial addition compound loses hydrogen halide and that the halogen then reacts on the newly formed unsaturated hydrocarbons. The reaction can be considered as taking place in the following stages:—

<sup>1</sup> See Chapter 54.

<sup>2</sup> F. Kirchhof, *Gummi-Ztg.*, 1932, 46, 497; *Chem. Abs.*, 1932, 26, 1827.



This last substance,  $(\text{C}_5\text{H}_4\text{Cl})_x$ , corresponds to a chlorine content of 68 per cent. The second phase of the reaction, as indicated, could take place with the formation of only one double bond, leading to a compound represented by the empirical formula  $(\text{C}_5\text{H}_4\text{Cl}_2)_x$ , and the presence of this material along with the final tetrahalogenated compound would account for the variation in the final products. As a matter of fact, derivatives containing approximately 70 per cent chlorine have been prepared.

McGavack<sup>a</sup> followed the chlorination reaction through its entire course by a method of gas analysis. The volume of chlorine passed into a solution of a known amount of rubber and the hydrogen chloride and unabsorbed chlorine coming off were measured by means of flowmeters. The results showed that substitution takes place almost exclusively during the early stages of the reaction but later diminishes in rate. Corresponding to the reduction in rate of substitution, the rate of addition increases accompanied by a gradual fall in temperature.<sup>a</sup> The final product has a chlorine content of approximately 65 per cent, which corresponds to that of a compound containing 3 substituted and 4 added chlorine atoms for each two  $\text{C}_5$  groups; thus  $(\text{C}_{10}\text{H}_{12}\text{Cl}_7)_x$  has 65.1 per cent chlorine content. In his experiments, McGavack also observed that the properties of the final product are influenced by the grade of rubber used, the type of apparatus, the intensity of light and the temperature of reaction. The course of the reaction and hence the chlorine content were found to be dependent, within limits, upon the type of solvent used and upon the temperature, substitution being favored by higher temperatures.

#### EARLY HISTORY OF HALOGENATION

Eck,<sup>b</sup> in a review of the early history of chlorinated rubber, called attention to the fact that the acid used by Fourcroy<sup>c</sup> (when the latter discovered that acids coagulate latex) was in fact chlorine water, the so-called oxidized muriatic acid.

<sup>a</sup> J. McGavack, *Ind. Eng. Chem.*, 1923, 15, 961.

<sup>b</sup> This is not inconsistent with the mechanism of Kirchhof, since the hydrogen chloride formed in that case also occurs in the initial stages of the reaction.

<sup>c</sup> L. Eck, *Gummi-Ztg.*, 1933, 47, 517; *Chem. Abs.*, 1933, 27, 2337.

<sup>d</sup> A. F. Fourcroy, *Ann. chim. phys.*, 1791, 11, 235. *Système des connaissances chimiques*, 1801, 8, 36.

For a long period rubber was thought to be resistant to chlorine; Berzelius,<sup>7</sup> for example, said that rubber tubes could be used in working with chlorine. Himly<sup>8</sup> reported the action of chlorine on the products of the destructive distillation of rubber and, in 1859, Traun<sup>9</sup> observed that chlorine, when passed into a solution of rubber in carbon disulphide, furnished a white substance which was no longer elastic or flexible.

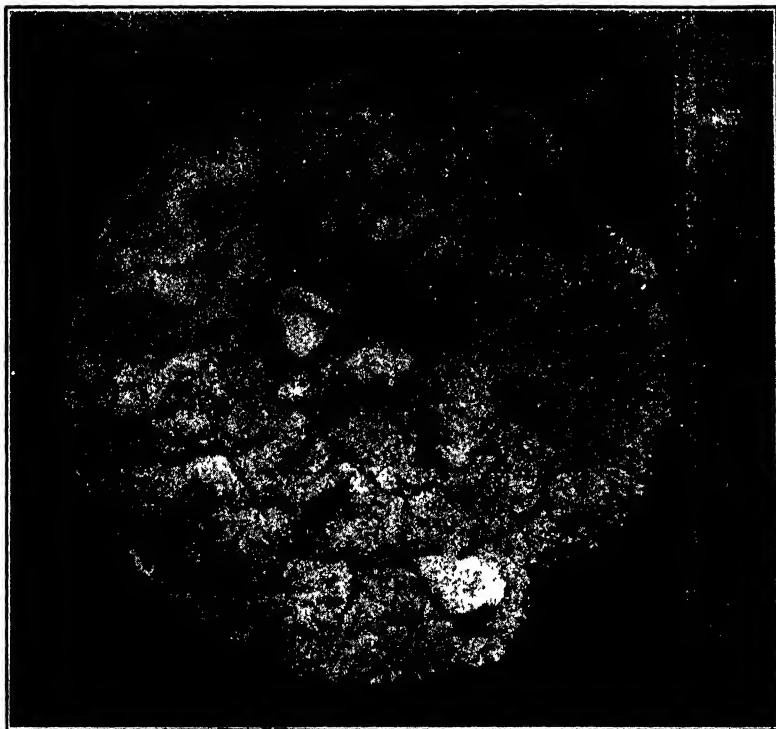


FIG. 142.—Spongy Form of Chlororubber. This piece, eleven inches in diameter and about three inches thick, weighs 295 grams.

In the same year, Engelhard and Havemann<sup>10</sup> described the effect of gaseous chlorine on solid rubber and on gutta-percha. The action of the gas on the solid was slow and was accompanied by swelling, yielding a brittle, white mass which, after washing out the chlorine with water, was soluble in the usual rubber solvents. Reaction was accelerated by using a solution of rubber in chloroform or benzene, from which the reaction product could be precipitated by alcohol as a hard, white mass, which was soluble also in carbon disulphide. The addition of zinc or calcium oxides to the chlorinated solution was stated to facilitate the preparation of hard bodies.<sup>11</sup>

Helm<sup>12</sup> immersed small pieces or thin sheets of either rubber or gutta-percha

<sup>7</sup> J. Berzelius, *Lehrbuch der Chemie*, 1839, 8, 23.

<sup>8</sup> Himly, *Dissertation Göttingen*, 1835.

<sup>9</sup> H. Traun, "Versuch einer Monographie des Kautschuks," Göttingen, 1859.

<sup>10</sup> G. A. Engelhard and R. F. H. Havemann, U. S. P. 25,175, Nov. 22, 1859. G. A. Engelhard and H. H. Day, *British P.* 2734, 1859.

<sup>11</sup> R. F. H. Havemann, U. S. P. 31,340 and 31,341, Jan. 29, 1861.

<sup>12</sup> J. Helm, Jr., U. S. P. 115,302, May 23, 1871.

in saturated chlorine water or in liquid chlorine and thus obtained a brittle mass which, after washing and drying, could be pressed in a hot mold. He found that a solution of rubber or gutta-percha in gasoline or benzene could be chlorinated by mixing with chlorine water or liquid chlorine (under pressure) and also suggested the addition of fillers (zinc oxide, Paris white, terra alba, ground glass or lime) before chlorination. The product was one of comparatively small chlorine content since the proportions used were about 3 parts of chlorine to 4 parts of rubber.

In subsequent studies made by Gladstone and Hibbert<sup>13</sup> chlorine was passed into a 1 per cent solution of rubber in chloroform exposed to diffused light. An immediate evolution of hydrogen chloride occurred and continued for a long period. Evaporation of the solvent yielded the chlorinated product in the form of yellowish scales. In every instance, both substitution and addition occurred and the best specimen contained 65.18 per cent of chlorine. Temperature had a definite effect on the course of the reaction.<sup>14</sup> Chlorination at 0°C. of a 1 per cent solution of rubber in benzene or chloroform yielded a product whose analysis (61.6 per cent of chlorine) approximated that which is represented by the formula,  $(C_{10}H_{14}Cl_2)_x$ .

#### CHLORINATION IN SOLUTION

Peachey<sup>15</sup> employed a method of chlorinating a 4 per cent solution of rubber in carbon tetrachloride. The mixture was agitated and cooled to absorb the heat generated during reaction, and chlorination was continued until the desired properties were obtained in the finished product. In this manner, chlororubber containing as much as 65 per cent chlorine could be prepared. Addition of camphor, either before or after chlorination, gave a material resembling leather. Peachey<sup>16</sup> also suggested the use of alkyl, alkylene and aryl halides as solvents and sulfuryl chloride or a mixture of bromine and chlorine as the halogenating agent. Corresponding reactions occur and similar products are formed when balata and gutta-percha are substituted for rubber. Even benzene and its homologues have been proposed as solvents,<sup>17</sup> the action of chlorine on the solvent being minimized by conducting the process in vessels made of stoneware or lead.

In another method, solutions of chlorine and rubber are mixed in the presence of water.<sup>18</sup> The latter absorbs the hydrogen chloride formed, thereby diminishing foaming and consequent loss of solvent. Further, if the water contains an oxidizing agent (sodium hypochlorite), the hydrogen chloride is oxidized returning chlorine to the reaction. The material finally obtained is an emulsion of water in chlorinated rubber solution.

The high viscosity of solutions of rubber in the customary solvents (which ordinarily limits concentrations to 3-5 per cent rubber) may be reduced by mastication of the rubber after it has been swollen in a solvent.<sup>19</sup> The viscosity of the chlorinated solution is particularly important when it is to be used as a varnish or lacquer since, as is well known, a paint of low viscosity is easier to apply. Rub-

<sup>13</sup> J. H. Gladstone and W. Hibbert, *J.C.S.*, 1888, 53, 679.

<sup>14</sup> F. W. Hinrichsen, H. Quensell and E. Kindscher, *Ber.*, 1913, 46, 1283; *Chem. Abs.*, 1913, 7, 2482.

<sup>15</sup> S. J. Peachey, U. S. P. 1,234,381, July 24, 1917; *Chem. Abs.*, 1917, 11, 2626. British P. 1894, 1915; *J.S.C.I.*, 1916, 35, 479.

<sup>16</sup> S. J. Peachey, British P. 121,091, 1917; *J.S.C.I.*, 1919, 38, 110A.

<sup>17</sup> H. M. Broadhurst, A. Lambie and S. J. Peachey, British P. 127,481, 1919, to United Alkali Company; *Chem. Abs.*, 1919, 13, 2467.

<sup>18</sup> D. F. Twiss and J. A. Wilson, British P. 414,862, 1934, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1935, 29, 640. French P. 772,782, 1934, to Soc. anon. des pneumatiques Dunlop; *Chem. Abs.*, 1935, 29, 1681.

<sup>19</sup> D. Spence and G. D. Kratz, *Kolloid-Z.*, 1914, 15, 217; *Chem. Abs.*, 1915, 9, 980.

ber that has been depolymerized by mastication, irradiation with ultraviolet light<sup>20</sup> or by the action of copper oleate<sup>21</sup> yields chlorinated products which dissolve to form solutions of relatively low viscosity. Dyche-Teague<sup>22</sup> employed a method in which rubber is milled and then dissolved to the extent of 10 per cent in carbon tetrachloride or a similar solvent. The product of chlorination after distilling off the solvent contains 50-60 per cent chlorine. A 20-30 per cent solution of this material in benzene had a viscosity about equal to that of linseed oil.

Preliminary oxidation of rubber to give it approximately 1 per cent combined oxygen offers a means of reducing the viscosity of solutions of its chlorinated products.<sup>23</sup> Oxidation may be brought about by heating rubber in thin sheets at 60°C. in air or oxygen, or by exposure of thin sheets to ozone, followed by milling. The effect may be obtained also by passing air, oxygen or ozone into rubber solutions<sup>24</sup> and by the addition of benzoyl peroxide or sodium hypochlorite.<sup>25</sup>

As the solutions in which rubber is chlorinated are usually fairly dilute, the problem of obtaining the solid chlorinated rubber remains. Spencer<sup>26</sup> recovered the solid product by passing the solution of rubber under the surface of an agitated heated liquid (in which the solvent was immiscible), the latter being maintained at a temperature above the boiling point of the solvent. As the chlororubber rose to the surface in a porous, spongy or fibrous condition, the solvent passed off as a vapor. When water is employed as the heating liquid, its boiling point may be increased, if necessary, by the addition of glycerol.<sup>27</sup> Another procedure involved spraying chlororubber solution into steam which was maintained near or above the boiling point of the solvent.<sup>28</sup> Steam and solvent vapor were removed simultaneously.

#### CHLORINATION OF SOLID RUBBER

Action of gaseous chlorine on solid rubber is slow and normally penetrates to only a slight depth because of the protective action of the superficial layer of chlorinated material. To offset this, Ellis<sup>29</sup> advocated masticating rubber in an atmosphere of chlorine. If desired a small amount of solvent is added as a plasticizing agent. The product may be used in solution as a lacquer or varnish base or mixed with fillers to form a molding composition.

Edison<sup>30</sup> recommended chlorination of thin rubber sheets by chlorine gas containing the vapors of carbon tetrachloride, the latter acting as a softening agent.

<sup>20</sup> N. Floresco, French P. 768,632, 1934; *Chem. Abs.*, 1935, 29, 640. See also British P. 416,252, 1934, to Chem. Fabrik Buckau; *Chem. Abs.*, 1935, 29, 1282. French P. 768,157, 1934; *Chem. Abs.*, 1935, 29, 640.

<sup>21</sup> B. V. Buizov, V. S. Molodenskii and N. I. Mikhailov, *J. Rubber Ind. (U.S.S.R.)*, 1934, 11, 44; *Chem. Abs.*, 1935, 29, 953.

<sup>22</sup> F. C. Dyche-Teague, U. S. P. 1,819,136, Aug. 18, 1931; *Chem. Abs.*, 1931, 25, 5797. British P. 305,968, 1927; *Brit. Chem. Abs. B*, 1929, 334.

<sup>23</sup> F. C. Dyche-Teague, U. S. P. 1,826,375, Oct. 6, 1931; *Chem. Abs.*, 1932, 26, 625. See also British P. 390,097, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1933, 481. French P. 744,565 and 751,535, 1933; *Chem. Abs.*, 1933, 27, 4439; 1934, 28, 1221.

<sup>24</sup> The simultaneous oxidation and chlorination of rubber has also been suggested. British P. 413,559, 1934, to Metallgesellschaft A.-G.; *Chem. Abs.*, 1935, 29, 376. French P. 764,391, 1934; *Chem. Abs.*, 1934, 28, 5714.

<sup>25</sup> British P. 421,313, 1934, to Chem. Fabr. Buckau; *Brit. Chem. Abs. B*, 1935, 197. French P. 773,431, 1934; *Chem. Abs.*, 1935, 29, 1631.

<sup>26</sup> W. D. Spencer, British P. 403,454, 1933, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 3260. J. P. Baxter (British P. 416,056, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 1281. French P. 769,806, 1934; *Chem. Abs.*, 1935, 29, 640) emulsified the solution in water before evaporating the solvent. See also British P. 413,069, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1935, 34.

<sup>27</sup> British P. 400,698, 1933, to Chemische Fabrik Buckau; *Chem. Abs.*, 1934, 28, 2319. French P. 758,280, 1934; *Chem. Abs.*, 1934, 28, 3269.

<sup>28</sup> French P. 761,001, 1934, to Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler; *Chem. Abs.*, 1934, 28, 4269. See also J. P. Baxter, British P. 419,723, 1933, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1935, 70.

<sup>29</sup> Carleton Ellis, U. S. P. 1,544,529, June 30, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1935, 19, 2789.

<sup>30</sup> T. A. Edison, U. S. P. 1,495,580, May 27, 1924; *Chem. Abs.*, 1924, 18, 2266.

The resulting soft mass contains some hydrogen chloride, which is removed by washing. Chlorination of powdered, unvulcanized rubber without the aid of a solvent is described by Martin.<sup>31</sup>

The greater solubility of chlorinated rubber has been utilized to accelerate chlorination of solid rubber. By suspending thin strips or sheets of rubber in carbon tetrachloride,<sup>32</sup> the solvent dissolves off the protective coat of chlorinated product during chlorination and thus exposes fresh rubber surfaces to the gas. In this manner a more rapid reaction is secured. The final product is a 32 per cent solution of chlorinated rubber in carbon tetrachloride. The dry chlororubber contains 70 per cent of chlorine. It was found more satisfactory to add the rubber gradually to the solvent as the reaction proceeded and it was necessary to stir the mass vigorously to insure complete contact. Temperatures between 50°C. and the boiling point of the solvent were employed. Additions of small amounts of bromine or iodine to the solution accelerated chlorination. Another catalyst which has been suggested is a Japanese acid clay.<sup>33</sup>

#### EFFECT OF TEMPERATURE ON CHLORINATION

Ellis<sup>34</sup> found that the reaction between chlorine and rubber suspended in a solvent was accelerated and a higher degree of chlorination favored as the temperature approached the boiling point of the solvent. The operation is most conveniently carried out in a closed vessel provided with reflux and an agitator. Iodine in the proportion of 1 g. per kg. of solvent is an effective catalyst. The product is light yellow and is readily soluble in benzene or in ethyl acetate and yields a hard, tough, glossy film on the evaporation of the solvent.

Chlorinated compounds prepared near the boiling point of the solvent<sup>35</sup> do not subsequently split off hydrogen chloride, are relatively acid free, and serve directly as film-forming ingredients in lacquers.<sup>36</sup>

#### CHLORINATION UNDER PRESSURE

By conducting chlorination at high pressures without the use of a solvent, some of the expense incident to handling solvent and unavoidable losses in its recovery may be obviated. At the same time the increased pressure overcomes the sluggish reaction between the gas and the solid rubber.

Experiments in the author's laboratory<sup>37</sup> have shown that, using a lead-lined autoclave loosely packed with thin sheet rubber, reaction proceeds very slowly at pressures below 60 pounds per square inch, yielding a product having only 30 per cent chlorine. At pressures above 60 pounds per square inch chlorination is much faster and is more nearly complete. Due to swelling of the mass, the capacity of the autoclave is limited.

<sup>31</sup> G. Martin, *Bull. Rubber Growers' Assoc.*, 1932, 14, 622; *Chem. Abs.*, 1933, 27, 628. For the use of soya-bean lecithin in the preparation of powdered rubber, see S. Minatoya and N. Kurahashi, *J. Soc. Chem. Ind., Japan*, 1934, 37, *Suppl. binding*, 207; *Chem. Abs.*, 1934, 28, 6024.

<sup>32</sup> Carleton Ellis, U. S. P. 1,544,529 and 1,544,530, June 30, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2759.

<sup>33</sup> T. Inokuchi, *Japanese P.* 95,117, 1932; *Chem. Abs.*, 1933, 27, 2843.

<sup>34</sup> Carleton Ellis, U. S. P. 1,544,532, June 30, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2759.

<sup>35</sup> Apparatus to be used in this type of reaction has been described by W. Beckmann, M. Desenise and A. Nielsen, U. S. P. 1,918,370, July 13, 1933, to New-York Hamburger Gummi-Waaren Co.; *Chem. Abs.*, 1933, 27, 4956. *British P.* 378,272, 1931; *Brit. Chem. Abs. B.*, 1932, 951. *British P.* 380,025, 1932, addn. to 378,272; *Brit. Chem. Abs. B.*, 1933, 481. *French P.* 725,700, 1931; *Chem. Abs.*, 1932, 26, 4981. *French P.* 41,880, 1933, addn. to 725,700; *Chem. Abs.*, 1933, 27, 4716.

<sup>36</sup> M. Desenise and A. Nielsen, U. S. P. 1,852,043, April 5, 1932, to New-York Hamburger Gummi-Waaren Compagnie; *Chem. Abs.*, 1932, 26, 3142. *British P.* 338,818, 1929; *Chem. Abs.*, 1930, 24, 5535. *German P.* 535,654, 1928; *Chem. Abs.*, 1933, 26, 4505.

<sup>37</sup> Carleton Ellis and N. Boehmer, U. S. P. 1,544,534, June 30, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2759.

A typical chlorination of this kind was carried out as follows: 100 grams of sheet rubber were loosely packed in a lead-lined autoclave and chlorine was introduced to bring the pressure to 80 lbs. per square inch. As the reaction proceeded, there was a slight rise in temperature, and the pressure gradually dropped in 16 hours to 50 lbs. per square inch. This pressure, caused largely by hydrogen chloride, was released and chlorine was re-introduced to 128 lbs. pressure. After each 24 hours this operation was repeated and at the end of 168 hours only an insignificant amount of hydrogen chloride was detected in the vented gas. Three hundred fifty seven g. of a white or light cream-colored mass containing 72 per cent of chlorine were isolated. Variations of the process were to omit venting hydrogen chloride if a low chlorine content was desired and to add chlorine continuously while venting at a rate slow enough to keep the pressure up to the desired point.

Liquid chlorine was found to be an effective chlorinating agent for solid rubber since it appears to be a good solvent for the reaction product.<sup>33</sup> Using an excess of chlorine at 70°C. and 323 lbs. pressure, chlorination was complete in 27 hours without any removal of hydrogen chloride. The product is a dark green viscous liquid from which, after reduction of the pressure, chlorine evaporates to yield a porous mass. On washing to remove hydrogen chloride and on drying this residue, a white or very light yellow material is obtained. It has been shown further that higher temperatures accelerate the reaction, but care must be exercised to prevent too much heating which discolors the product.<sup>33</sup> Another modification employs rubber which has been masticated with a small amount of solvent, furnishing (as has been noted above) a material which forms solutions of low viscosity.<sup>40</sup>

#### NEUTRALIZING AGENTS (ANTACIDS)

Inasmuch as chlorination is accompanied by the evolution of hydrogen chloride, it is necessary that acid be completely removed from the product before use. Even the greatest care in this respect does not prevent the generation of hydrogen chloride by the subsequent slow decomposition of highly chlorinated products. At elevated temperatures this decomposition may become rapid. To offset the tendency to split off hydrogen chloride, it has been found that the addition of basic compounds, e.g., aniline, toluidine and xylylene, diphenylamine, phenylene diamine and urea, are effective in stabilizing chlorinated rubber solutions.<sup>41</sup> On the other hand, the oxides of zinc, barium and magnesium may be used in pigmented paints and lacquers where solubility of the stabilizer in the mix is not essential.

A stabilized product is obtained by chlorinating rubber in carbon tetrachloride solution in the presence of sodium carbonate or potassium bicarbonate. When 55-65 per cent of chlorine has combined, the solution is heated to boiling for several hours.<sup>42</sup> Thus prepared, the material does not yield hydrogen chloride when heated up to about 180°C.<sup>42</sup> Another class of stabilizing agents includes the derivatives of ethylene oxide, (epichlorohydrin, phenoxypropene oxide, dimethylglycidol and phenylmethylglycidol).<sup>43</sup> Becker and Blömer<sup>44</sup> isolated chlororubber from solution in carbon tetrachloride by pouring the reaction mixture into alcoholic

<sup>33</sup> Carleton Ellis and N. Boehmer, U. S. P. 1,544,535, June 30, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2759. Canadian P. 273,676, 1927; *Chem. Abs.*, 1927, 21, 4098.

<sup>39</sup> Carleton Ellis and N. Boehmer, U. S. P. 1,544,531, June 30, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2759.

<sup>40</sup> Carleton Ellis, U. S. P. 1,695,636, Dec. 18, 1928, to Chadeloid Chemical Co.; *Chem. Abs.*, 1929, 23, 1013.

<sup>41</sup> Carleton Ellis, U. S. P. 1,695,641, Dec. 18, 1928, to Chadeloid Chemical Co.; *Chem. Abs.*, 1929, 23, 1012.

<sup>42</sup> British P. 381,098, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1932, 1044. French P. 782,434, 1932; *Chem. Abs.*, 1932, 27, 1783. An alternative method involves heating solutions of chlorinated rubber while they are emulsified with aqueous alkali. British P. 418,068, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1933, 34.

<sup>43</sup> British P. 358,154, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1933, 30.

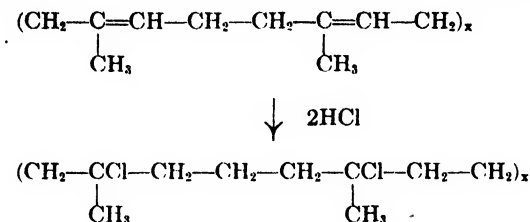
<sup>44</sup> French P. 755,490, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1571. British P. 418,320, 1933; *Brit. Chem. Abs. B.*, 1935, 12.

<sup>45</sup> W. Becker and A. Blömer, U. S. P. 1,933,912, Mar. 12, 1935, to I. G. Farbenind. A.-G.

potassium hydroxide. The product precipitated as a powder which was then stabilized by stirring at room temperature for 15-20 hours.

### RUBBER HYDROCHLORIDE

Rubber in solution reacts with hydrogen chloride to form substances simulating those formed by chlorine. The reaction may be expressed as follows:



Harries<sup>46</sup> prepared a compound corresponding to  $(\text{C}_{10}\text{H}_{16}\text{Cl}_2)_x$  by saturating solutions of rubber<sup>47</sup> in chloroform or benzene with hydrogen chloride and allowing them to stand 12 hours. The product, precipitated from solution by addition of alcohol, is white and elastic, becoming brittle on standing. It is soluble in benzene and chloroform but insoluble in ether and alcohol. It has no characteristic melting point; decomposition beginning at 145°C. becomes complete at 185°C. Treatment with pyridine or with sodium hydroxide solution removes hydrogen chloride from the compound, yielding a chlorine-free rubber. Weber<sup>48</sup> stated that moisture is necessary to the formation of a resinous hydrochloride and that without its presence sticky masses are formed. He further noted the partial decomposition of rubber hydrochloride when treated with organic bases and found that although hydrogen chloride splits off on heating, an amount of chlorine corresponding to about 18 per cent is held tenaciously even up to 100°C., indicating a stable compound of this composition.

Oenslager<sup>49</sup> proposed using a solvent for hydrogen chloride which did not dissolve rubber, e.g., ethyl acetate and similar esters.<sup>50</sup> Ethyl acetate exerts merely a softening action on rubber and dissolves as much as 20 per cent of dry hydrogen chloride. The procedure consists of immersing thin sheets of masticated rubber in a saturated solution of hydrogen chloride in ethyl acetate at room temperature for 36-48 hours. The product retains the shape of the original sheets and possesses a deep-amber, translucent, horny appearance. It is tough and hard and much more resistant than rubber to destructive agencies including oxidizing acids and the hydrocarbons, gasoline, kerosene and lubricating oil.<sup>51</sup>

Rubber will add hydrogen fluoride until a content of 30 per cent of fluorine is attained. Heat, however, decomposes this material and a plastic body containing about 2 per cent of fluorine results. The softening point of the product depends on the concentration of the acid employed. For example, the action of 69

<sup>46</sup> C. Harries and E. Fonrobert, *Ber.*, 1913, 46, 733; *J.S.C.I.*, 1913, 32, 372. See also F. W. Hinrichsen, H. Quensell and E. Kindscher, *Ber.*, 1913, 46, 1283; *Chem. Abs.*, 1913, 7, 2482.

<sup>47</sup> As was noted above, if plasticized rubber is employed, more concentrated solutions are possible. H. I. Waterman, C. G. H. Max and J. J. Leendertse, *Chem. Weekblad*, 1934, 31, 614; *Brit. Chem. Abs.*, B, 1935, 70.

<sup>48</sup> C. O. Weber, *Ber.*, 1900, 33, 789; *J.C.S.*, 1900, 78 (1), 354.

<sup>49</sup> G. Oenslager, U. S. P. 1,841,295, Jan. 12, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1932, 26, 1829.

<sup>50</sup> Cf. the preparation of rubber hydrochloride in the absence of a solvent, E. Gebauer-Fuelnegg and E. W. Moffett, U. S. P. 1,980,396, Nov. 13, 1934, to Marsene Corp. of America; *Chem. Abs.*, 1935, 29, 376.

<sup>51</sup> Films and filaments of rubber hydrochloride are reported to be durable. H. I. Waterman, C. G. H. Max and J. J. Leendertse, *loc. cit.* Cf. the preparation of transparent wrapping sheets, W. C. Calvert, U. S. P. 1,989,682, Jan. 29, 1935, to Wingfoot Corp.; *Chem. Abs.*, 1935, 29, 2023. French P. 767,326, 1934; *Chem. Abs.*, 1935, 29, 376.



and 85 per cent solutions on smoked sheets gives bodies softening at 90° and 155°C. respectively. Further, the more concentrated acid reacts faster, requiring only 6 hours as compared with 48 for the other.<sup>52</sup>

Ellis<sup>53</sup> devised a method for treating rubber with chlorine and hydrogen chloride in a series of reaction vessels. Each vessel is charged with the mixture of gases vented from the one above it. Chlorine is introduced into the first and, when the material in this is ready to be removed, a fresh vessel is inserted at the bottom of the series.

#### ACTION OF HYPOCHLOROUS ACID

Hypochlorous acid, like hydrogen chloride, adds to an unsaturated linkage and has found use in the halogenation of rubber. Inasmuch as hypochlorous acid is relatively un-ionized, it does not effect coagulation of the latex. The acid may be formed *in situ*, by passing chlorine directly into latex previously made alkaline with sodium carbonate. The first product formed according to Bloomfield and Farmer<sup>54</sup> was a light, fine, pale-yellow powder which approximated  $C_5H_7OCl$  in composition. Further treatment of latex with hypochlorous acid resulted in the replacement of hydrogen atoms by chlorine. When the chlorine content approached 45.8 per cent, the material was an insoluble, cream-colored powder. Not being coagulated by heat or acid, further chlorination was resorted to at 80-100°C. under acid conditions. With one sample of Malay latex the product was a white powder containing 51.1 per cent chlorine and was soluble in chloroform, cyclohexanone, cyclohexyl acetate and diacetone alcohol.

Agitation of rubber solutions with aqueous solutions of hypochlorous acid at 0-5°C. results not only in chlorination of the rubber but also addition of the acid, provided at least one molecular proportion of the latter is employed. The highest degree of chlorination was accomplished in chloroform solution by a 3-day treatment with 5 molecular proportions of hypochlorous acid. The product was a fine, white powder, soluble in chloroform, benzene and acetone, but insoluble in carbon tetrachloride. Analysis showed 66.0 per cent chlorine and 8.5 per cent hydroxyl. These proportions approximate the formula,  $(C_5H_7OCl_5)_x$ .

#### BROMINATION AND IODINATION

The action of bromine and iodine on rubber is somewhat analogous to that of chlorine and in most of the chlorination procedures either of these may be substituted. In general, the products formed are darker in color than the chlorine derivatives and it is difficult to introduce as large an atomic proportion of either bromine or iodine into the rubber molecule. It should be noted that the bromine and iodine compounds of rubber are much less soluble than the corresponding chlorine derivative. The catalytic effect of iodine on the chlorination of rubber has already been noted above. Rubber, gutta-percha and balata all add iodine monobromide and iodine monochloride. A solution of the latter was recommended by Kemp and Mueller<sup>55</sup> as a reagent for measuring the degree of unsaturation of rubber.

<sup>52</sup> British P. 414,425, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 522. French P. 750,500, 1933; *Chem. Abs.*, 1934, 28, 931.

<sup>53</sup> Carleton Ellis, U. S. P. 1,544,533, June 30, 1925, and 1,695,636, Dec. 18, 1928, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2759; 1929, 23, 1013. Cf. the chlorination of rubber hydrochloride, C. E. Bradley and W. A. Gibbons, U. S. P. 1,627,725, May 10, 1927, to Naugatuck Chem. Co.; *Chem. Abs.*, 1927, 21, 3200.

<sup>54</sup> G. F. Bloomfield and E. H. Farmer, *J.S.C.I.*, 1934, 53, 43T, 47T. See also A. D. Luttringer, *Caoutchouc et gutta-percha*, 1934, 31, 16829, 16861; *Chem. Abs.*, 1934, 28, 6589.

<sup>55</sup> A. R. Kemp and G. S. Mueller, *Ind. Eng. Chem., Anal. Ed.*, 1934, 6, 52. See also R. Punniemer and F. J. Mann, *Ber.*, 1929, 62, 2636; *Brit. Chem. Abs. A*, 1929, 1455.

Bromine reacts directly on a chloroform solution of rubber. Hydrogen bromide is evolved and compounds of variable composition, approximating the formulas,  $(C_{10}H_{18}Br)_x$  and  $(C_{10}H_{15}Br)_x$ , are obtained.<sup>56</sup> Weber<sup>57</sup> prepared the tetrabromide of rubber and found it to resemble closely the corresponding chlorine compound. The rubber tetrabromide reacted readily with sodium ethylate presumably by the substitution of ethoxy groups for bromine.

A tetraphenoxy derivative of rubber was formed by adding rubber tetrabromide to molten phenol.<sup>58</sup> At 60°C., hydrogen bromide was evolved yielding a red-violet solution from which could be recovered an ochre-colored, pulverulent material, readily soluble in aqueous or alcoholic sodium hydroxide, alcohol, acetone, ether and ethyl acetate, but insoluble in benzene, chloroform, carbon disulphide and petroleum ether. Later this compound was shown to be 4,4'-dihydroxydiphenyldihydorrubber<sup>59</sup> since it can be methylated to form a dimethoxy derivative.<sup>60</sup> An analogous material produced at 90-95°C. appeared to be a tetraphenoxy-dihydroxy derivative. Compounds of this type split off phenol, however, when heated with sodium hydroxide solution.

The reaction of rubber with the halogens was at one time deemed to be practically the same as that of vulcanization with sulphur, but further study of the two series of derivatives has shown this view to be no longer tenable. Pearson,<sup>61</sup> for example, stated that rubber dipped in bromine was "vulcanized" immediately. A mixture of one part bromine and two parts iodine could be used for the same purpose, a hard compound being obtained when the treatment took place at 121°C. Likewise hypochlorite solutions were employed for the same purpose.<sup>62</sup>

Although Gladstone and Hibbert<sup>63</sup> reported no action between iodine and rubber in solution, Weber<sup>64</sup> obtained a compound corresponding to  $(C_{10}H_{18}I)_x$  by treating a rubber solution with iodine for 2 days. Iodine addition products could be obtained in chloroform solution by the catalytic action of sunlight.<sup>64</sup> A so-called "vulcanized" rubber results when a solution of 10 parts of rubber in carbon tetrachloride is treated with 1 part iodine dissolved in the same solvent.<sup>65</sup> A similar compound was prepared by Rasser.<sup>66</sup>

Hydrogen bromide forms addition compounds with rubber similar to those of hydrogen chloride, according to both Harries<sup>67</sup> and Hinrichsen, Quensell and Kindscher.<sup>68</sup> The latter obtained a compound corresponding to  $(C_{10}H_{18}Br)_x$ .

Although addition compounds of hydrogen iodide and rubber are much less stable, a di-iodo derivative corresponding to  $(C_{10}H_{18}I)_x$  has been prepared; this compound readily loses a molecule of hydrogen iodide.<sup>69</sup> Hinrichsen, Quensell and Kindscher<sup>70</sup> confirmed this observation concerning instability and were able to isolate with certainty only one compound corresponding to  $(C_{10}H_{17}I)_x$ .

<sup>56</sup> J. H. Gladstone and W. Hibbert, *J.C.S.*, 1888, 53, 679.

<sup>57</sup> C. O. Weber, *Ber.*, 1900, 33, 786; *J.C.S.*, 1900, 78 (1), 354. See also F. W. Hinrichsen, H. Quensell and E. Kindscher, *loc. cit.*

<sup>58</sup> C. O. Weber, "The Chemistry of India Rubber," Griffin and Co., London, 1912, 33. See also *Ber.*, 1900, 33, 791; *J.C.S.*, 1900, 78 (1), 355.

<sup>59</sup> The name "tetraphenoxy rubber" was based on the formulation of rubber as  $C_{10}H_{16}$  and not as a  $C_8H_8$  unit.

<sup>60</sup> H. L. Fisher, H. Gray and E. M. McColm, *J.A.C.S.*, 1926, 48, 1309. See also E. Geiger, *Helv. Chim. Acta*, 1927, 10, 530; *Brit. Chem. Abs. A*, 1927, 870.

<sup>61</sup> H. C. Pearson, "Crude Rubber and Compounding Ingredients," 1909, 72.

<sup>62</sup> C. O. Weber, "The Chemistry of India Rubber," Griffin & Co., London, 1912, 55.

<sup>63</sup> J. H. Gladstone and W. Hibbert, *J.C.S.*, 1888, 53, 679.

<sup>64</sup> C. O. Weber, *Ber.*, 1900, 33, 788; *J.C.S.*, 1900, 78 (1), 354.

<sup>65</sup> F. W. Hinrichsen and R. Kempf, *Ber.*, 1913, 46, 1237; *Chem. Abs.*, 1913, 7, 2482. They mention that H. Quensell used phosphorus as a catalyst.

<sup>66</sup> H. Scherpe, U. S. P. 906,304, Dec. 8, 1908, to Degan and Kuth. *British P.* 9956, 1908; *J.S.C.I.*, 1909, 28, 52.

<sup>67</sup> E. O. Rasser, *Kunststoffe*, 1923, 13, 18; *Chem. Abs.* 1924, 18, 2617.

<sup>68</sup> C. Harries, *Ber.*, 1913, 46, 733; *Chem. Abs.*, 1913, 7, 2862.

<sup>69</sup> F. W. Hinrichsen, H. Quensell and E. Kindscher, *loc. cit.*

<sup>70</sup> C. Harries, *loc. cit.*

<sup>71</sup> F. W. Hinrichsen, H. Quensell and E. Kindscher, *loc. cit.*

Kirchhof<sup>71</sup> treated the sulphuric acid transformation products of rubber with bromine and obtained  $(C_{20}H_{30}Br_2)_x$ . These sulphuric acid transformation products are made by the action of concentrated sulphuric acid on solutions of raw rubber in carbon tetrachloride. Similar treatment of pale crêpe rubber yields a brittle red powder which is probably an oxidation product.

#### OTHER VARIETIES OF RUBBER

Thus far methods intended primarily for the preparation of halogen derivatives of rubber have been discussed. By rubber is meant the usual standard grade obtained from the tree, *Hevea brasiliensis*, and known as "pale crêpe" or "plantation para rubber." However, rubber latex, chicle, balata, gutta-percha and other grades and types of materials or artificial rubber may be used similarly. Reaction between halogens and such rubber-like materials are analogous to those of rubber itself. Chlorinated gutta-percha, for instance, resembles chlorinated rubber but possesses a somewhat yellow color.

The use of chlorinated balata or gutta-percha to provide a tough, flexible, nonflammable insulation for electrical conductors was advocated by Edison in 1890.<sup>72</sup> His procedure was to treat a solution of the material in a solvent unaffected by chlorine until a dried film of the treated substance was somewhat brittle and nonflammable. The desired degree of flexibility could be obtained by mixing the product with some of the raw material.

The addition compounds of gutta-percha with the hydrogen halides,<sup>73</sup> when treated with pyridine or sodium hydroxide solution, decompose into substances more closely resembling rubber than the parent substance. Gutta-percha dihydrochloride  $(C_{10}H_{12}Cl_2)_x$ , is tough when freshly made but becomes brittle on standing. Decomposition, with the evolution of hydrogen chloride, occurs at 170°C.; at 200°C. there is a complete breakdown.

#### VULCANIZED AND RECLAIMED RUBBER

Chlorination of vulcanized rubber is complicated by its insolubility in the usual solvents for raw rubber and also by the presence of sulphur or other vulcanizing agents. Bedford and Kelly<sup>74</sup> suggested a process consisting of, first, removing excess sulphur by extracting with acetone or with caustic alkali, suspending the material in carbon tetrachloride and then treating the suspension with gaseous chlorine. To increase the solubility of rubber after removal of the excess vulcanizing agent it is plasticized at 150-170°C. with a high-boiling solvent (pine oil, aniline, nitrobenzene and acetylene tetrachloride). The high-boiling solvent is removed by repeated dilution, and the rubber is precipitated with lower-boiling solvents and finally chlorinated in carbon tetrachloride, after first removing mineral fillers and pigments. The addition of sulphur (2 per cent) or sulphur chloride to a solution of raw rubber in carbon tetrachloride before chlorination is reported to yield a product similar to that from vulcanized rubber. Varnishes, lacquers and a thermoplastic molding material can be produced by chlorinating rubber in carbon tetrachloride solutions which contain more than 5 per cent of sulphur.<sup>75</sup>

<sup>71</sup> F. Kirchhof, *Kolloid-Z.*, 1922, 30, 176; *Chem. Abs.*, 1922, 16, 1885. See Chapter 54.

<sup>72</sup> T. A. Edison, U. S. P. 433,809, Oct. 14, 1890.

<sup>73</sup> C. Harries, *loc. cit.*

<sup>74</sup> C. W. Bedford and W. J. Kelly, U. S. P. 1,377,152, May 3, 1921, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1921, 15, 2749.

<sup>75</sup> D. F. Twiss and J. A. Wilson, British P. 410,349, 1932, and 410,370, 1933, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs. B*, 1934, 640. French P. 766,289, 1934, to Soc. anon. des pneumatiques Dunlop; *Chem. Abs.*, 1934, 28, 7562. The liquid polychlorides of benzene have also been utilised as solvents, M. Polunkovskaya, *J. Rubber Ind. (U. S. S. R.)*, 1934, 11, 142; *Chem. Abs.*, 1934, 28, 7569.

Benzene may be used as the solvent and no difficulty encountered from the action of chlorine on it even when chlorination is conducted at temperatures near the boiling point of the liquid. In variations of the method, chlorination was accompanied by vulcanization with sulphur chloride or it was preceded by treatment with hydrogen chloride.<sup>76</sup> Hard rubber dust, after being freed from excess sulphur, yielded on chlorination a dark brown liquid.

Ellis and Boehmer<sup>77</sup> chlorinated vulcanized rubber by the application of pressure without the use of a solvent and obtained a product practically insoluble in benzene and considerably tougher than raw rubber similarly treated. The Deseniess and Nielsen<sup>78</sup> method of chlorinating raw rubber in boiling carbon tetrachloride was equally applicable to vulcanized rubber, as all of the sulphur was removed as sulphur chloride during the reaction.

Harries<sup>79</sup> has proposed a method of regenerating vulcanized rubber by treating it with hydrogen chloride. A thick, colloidal solution of rubber in xylene is saturated with hydrogen chloride and the rubber hydrochloride formed is then refluxed with pyridine or is added to fused sodium or potassium hydroxide. The regenerated rubber is oily, but polymerization causes it to increase in consistency on standing.

Products which are more soluble than ordinary chlorinated rubber have been made by Shadbolt<sup>80</sup> through treatment of the thermoplastic substances produced from rubber by the action of oxygenated phosphorus halides which contain more oxygen than the corresponding phosphorus oxyhalides. Even though many plasticizers may be mixed with the products, vegetable oils are incompatible.

#### USE OF CHLORINATED RUBBER AS A PAINT

Aside from use to a limited extent as a molding compound, the important application of chlorinated rubber has been in the field of lacquers and protective coatings.<sup>81</sup> The fact that inexpensive solvents can be employed has contributed to this development. The clarity and light color of the finished film and the low viscosity of solutions of relatively high concentration make its application for this purpose particularly desirable. A benzene solution containing as much as 20-30 per cent of highly chlorinated rubber has a good brushing consistency whereas a similar solution containing 6 per cent of crude rubber will scarcely pour.<sup>82</sup> The dried film from a chlorinated product of this kind is hard, tough, glossy and trans-

<sup>76</sup> C. E. Bradley and W. A. Gibbons, U. S. P. 1,627,725, May 10, 1927, to Naugatuck Chemical Co.; *Chem. Abs.*, 1927, 21, 2200.

<sup>77</sup> Carleton Ellis and N. Boehmer, U. S. P. 1,544,534, June 30, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2759.

<sup>78</sup> M. Deseniess and A. Nielsen, U. S. P. 1,852,043, April 5, 1932, to New-York Hamburger Gummi-Waaren Compagnie; *Chem. Abs.*, 1932, 26, 3142. British P. 228,818, 1929; *Chem. Abs.*, 1930, 24, 5535. German P. 535,054, 1928; *Chem. Abs.*, 1932, 26, 4505.

<sup>79</sup> C. Harries, German P. 267,277, 1912; *J.S.C.I.*, 1914, 33, 93.

<sup>80</sup> F. S. Shadbolt, British P. 390,154, 1933; *Chem. Abs.*, 1934, 28, 686.

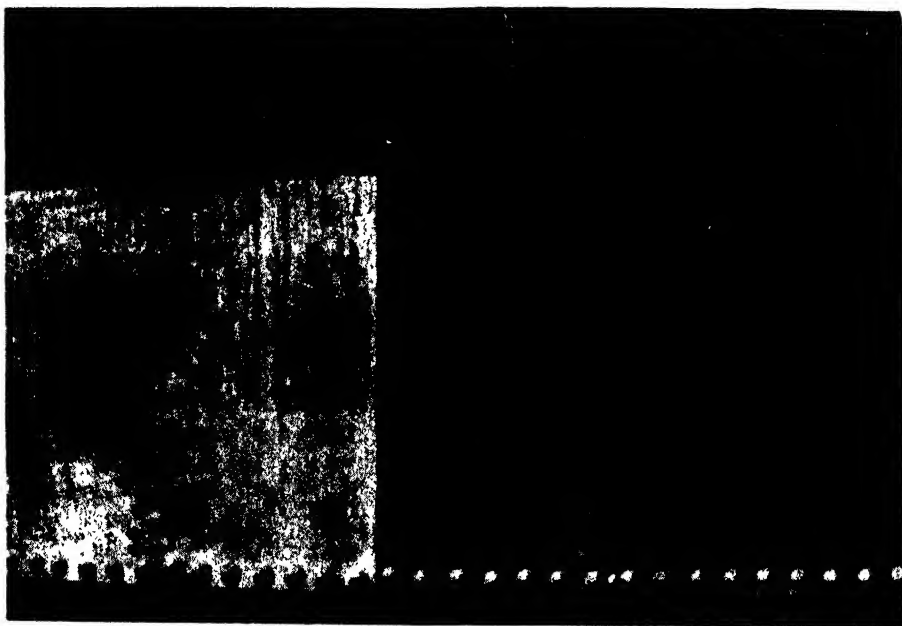
<sup>81</sup> Reviews on the use of chlorinated rubber as a paint or lacquer have been contributed by: F. Kirchhof, *Gummi-Ztg.*, 1932, 46, 497; *Chem. Abs.*, 1932, 26, 1827. O. Merz, *Farbe u. Lack*, 1932, 281, 295; *Chem. Abs.*, 1932, 26, 4731. A. Nielsen, *Kautschuk*, 1933, 9, 167; *Chem. Abs.*, 1934, 28, 663. Oesterr. *Chem. Ztg.*, 1933, 36, 192; *Brit. Chem. Abs. B*, 1934, 158. *Chem. Age*, 1921, 4, 508. *India Rubber World*, 1922, 66; *Kunststoffe*, 1922, 12, 43. *Synthetic and Applied Finishes*, 1934, 5, 83, 98. *Chem. Met. Eng.*, 1932, 39, 876. L. Borodulin, *J. Rubber Ind. (U. S. S. R.)*, 1934, 11, 203; *Chem. Abs.*, 1935, 29, 637. K. Buser, *Farben-Ztg.*, 1934, 39, 1240, 1263; *Chem. Abs.*, 1935, 29, 1267. J. H. Frydlander, *Rubber Age (London)*, 1933, 14, 13; *Chem. Abs.*, 1933, 27, 2887. C. F. A. Kappelmeyer, *Chem. Weekblad*, 1934, 31, 423; *Brit. Chem. Abs. B*, 1934, 772. F. Marchionna, *Rubber Age (N. Y.)*, 1934, 36, 71, 129; 1935, 36, 185; *Chem. Abs.*, 1935, 29, 953, 2025. J. M. Fain, *Metal Cleaning and Finishing*, 1935, 7, 117; *Chem. Abs.*, 1935, 29, 4100.

<sup>82</sup> J. G. Fol and A. B. Bijl, *Bull. Rubber Growers' Assoc.*, 1932, 14, 210; *Chem. Abs.*, 1932, 26, 3968. See also Carleton Ellis and N. Boehmer, U. S. P. 1,544,534, June 30, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2759.

lucent with a light yellow color and exhibits a high resistance to the action of acids, alkalis and oxidizing agents.<sup>81</sup>

#### PROPERTIES OF CHLORINATED RUBBER PAINTS

Tornesit represents the first commercial recognition in the United States of the value of chlorinated rubber. The manufacture of Tornesit began in Germany at a place called Tornesch, near Hamburg. Later, an American concern,<sup>82</sup> after a



*Courtesy Hercules Powder Company*

FIG. 143.—Comparison of Tornesit (lower right) with Two Other Acid-Resisting Paints After Exposure for Two Years.

protracted investigation, embarked on the manufacture of Tornesit in the United States.<sup>83</sup> As a result of these tests Tornesit is considered to be "probably the most important development in the protective-coating industry since the discovery of nitrocellulose as a base for lacquers." Considered from the standpoint of commercial utility, it seems likely that no other film approaches Tornesit in resistance to acids, alkalis and the many other corrosive elements that are normally destructive to coatings. It gives to the paint manufacturer a material that can be formulated into both an acid- and alkali-resisting paint. Its general uses in protecting property against corrosion, weathering, water, steam, dust, fumes, gas, alkalis and acids become more widespread as its advantages become more generally known.<sup>84</sup>

<sup>81</sup> Chlorinated rubber has been placed on the market under the trade names "Duoprene" (United Alkali Co., I. Levinstein & Co., Imperial Chem. Ind., Ltd.), "Pergut" (I. G. Farbenind. A.-G.), "Tornesit" (New-York Hamburger Gummi-Waaren Compagnie, "Herold" A.-G.; Deutsche Tornesit-G.m.b.H., Hercules Powder Co.) and "Tegofan" (Tegofan G.m.b.H.).

<sup>82</sup> Hercules Powder Co., Wilmington, Del.

<sup>83</sup> License rights were secured by the Hercules Powder Co. from the German company and also from the Chadeloid Chemical Co., owners of the Ellis and Boehmer U. S. Patents

<sup>84</sup> For reports on Tornesit see D. R. Wiggam, W. Koch and F. Mayfield, *Ind. Eng. Chem., News*

Tornesit is practically odorless, non-inflammable and non-combustible. The specific gravity is about 1.5 and the product yields a bulking value, when put into solution, of 0.08 gallon per pound, which is about that of nitrocellulose. When Tornesit solution is poured on a glass plate and allowed to dry, a clear film similar to nitrocellulose results. The toughness of the film varies with the viscosity of the Tornesit used, but the grade useful in protective coatings is quite brittle and requires compounding with softening agents to impart the necessary flexibility.

Tornesit of widely differing viscosities may be prepared.<sup>87</sup> The 130-centipoise type is most useful in protective coatings, permitting spraying and brushing concentrations similar to those attainable with  $\frac{1}{4}$ -second nitrocellulose. The 130-centipoise viscosity was determined on a 20 per cent solution of Tornesit and toluene with the capillary viscosimeter at 25°C. This material closely parallels the viscosity of  $\frac{1}{4}$ -second nitrocellulose in a mixture of 50 per cent butyl acetate and 50 per cent toluene. For plastics or fabric coating, where greater toughness is desired, higher viscosity types are useful, but for adhesives lower viscosity grades are valuable.

#### SOLVENTS AND PLASTICIZERS OF CHLORINATED RUBBER PAINTS

Tornesit is insoluble in water, but dissolves readily in the common aromatic hydrocarbons (benzene, toluene, xylene), although completely insoluble in petroleum hydrocarbons.<sup>87a</sup> The chlorinated aliphatic hydrocarbons (ethylene dichloride and carbon tetrachloride), however, are good solvents. Tornesit is not soluble in either aliphatic or aromatic alcohols. Ethyl ether has a slight swelling action. On the other hand, ethylene glycol, glycerol diethyl ether and certain other ethers of glycerol<sup>88</sup> are good solvents. Ketones behave like ethyl ether in producing a swelling action. Along with the ethers, the ketones may be used as diluents to confer the special evaporation rate required of the solvent mixture. All of the common ester solvents may be used with Tornesit.<sup>89</sup> The terpene hydrocarbons are in general incompatible; on blowing with air, they become swelling agents and in some cases active solvents. Alkyl sulphides, sulfoxides, and sulphones are excellent solvents.

Table 57 indicates the types of softening agents which are especially useful:

TABLE 57.—*Tornesit Plasticizers.*

Types	Examples
Drying oils.....	{ Linseed oil Tung oil Soya bean oil
Non-drying oils.....	{ Raw Castor oil Palm oil
Fatty acid esters.....	{ Butyl stearate Amyl stearate
Hydrogenated or unhydrogenated alkyl or aralkyl esters of abietic acid.....	{ Hercolyn <sup>90</sup>
Adipic acid esters.....	Sipalins
Phthalic acid esters.....	Dibutyl phthalate
Phosphoric acid esters.....	{ Triphenyl phosphate Tricresyl phosphate
Citric acid esters.....	Triethyl citrate
Chlorinated aromatic compounds.....	Aroclors

*Ed.*, 1934, 12, 179. R. A. Coolahan, *J.S.C.I.*, 1934, 53, 630; *Official Digest Fed. Paint, Varnish Prod. Clubs*, 1934, 133, 30; *Rubber Age*, 1934, 35, 17; *Chem. Abs.*, 1934, 28, 2550, 3616.

<sup>87</sup> Tornesit solutions with viscosities of 30, 130 and 500 centipoises are commercially available.

<sup>87a</sup> See F. Kirchhof, *Chem.-Ztg.*, 1934, 58, 542; *Brit. Chem. Abs. B*, 1934, 774.

<sup>88</sup> Epiethylin and epiphenylin.

<sup>89</sup> Tests made on 25 cc. of 20% toluol solutions of Tornesit show that the following amounts of diluents will be tolerated before precipitation occurs: Union Solvent #8=26.7cc.; Union Solvent #20=75.0 cc.; Union Solvent #30=75.0 cc.; Union Solvent #40=150.0 cc.; Solvesso #1=31.0 cc.; V. M. & P. Naphtha=19.4 cc.

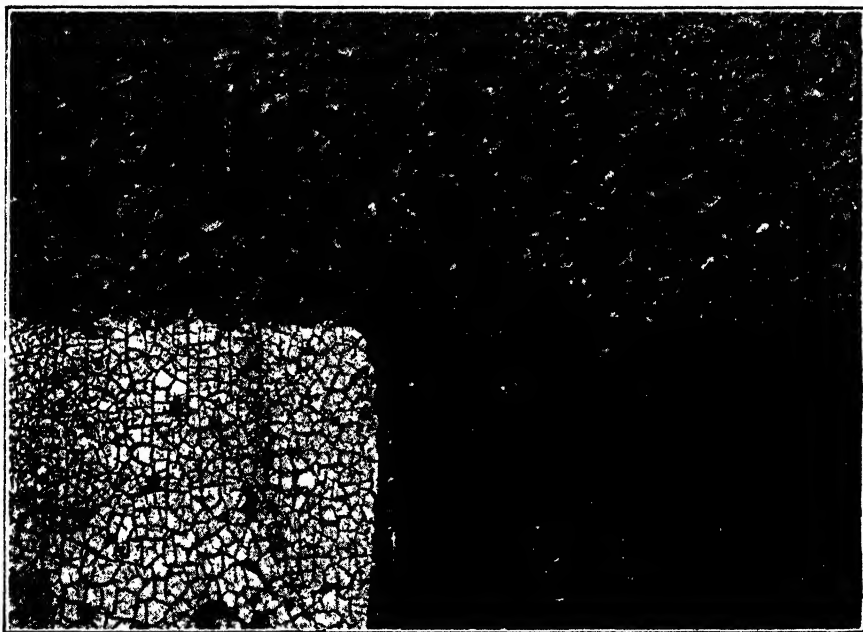
<sup>90</sup> The ethyl ester of hydrogenated abietic acid.

Tornesit was found to be compatible in films with the following substances<sup>a</sup> when both were dissolved in a mutual solvent, and a film was produced from this solution: raw castor oil, raw tung oil, bodied tung oil, pine tar, gas-house tar, rosin, ester gum, elemi, dammar, copals, amberols, cumarones, indenes and certain of the polyvinyls,<sup>b</sup> polyacrylins and bitumens.<sup>c</sup>

By the same method, the following materials were found to be less compatible or incompatible: bodied castor oil, rubber, Resoglas,<sup>d</sup> gilsonite, ethyl cellulose, benzyl cellulose, butyl cellulose, cellulose nitroacetate, asphalt, coal tar, Paraplex RG-2,<sup>e</sup> nitrocellulose, benzyl ether resin, vaseline, Nujol, vinylite resins and most of the phthalic anhydride resins tested.

#### FORMULATION OF CHLORINATED RUBBER PAINTS

Extraordinary adhesion is imparted to a Tornesit film by various plasticizers, a good combination being bodied tung oil and Hercolyn. Good adhesion also re-



*Courtesy Hercules Powder Company*

FIG. 144.—Closeup of Fig. 143.

sults from the incorporation of soft resins and pigments into plasticized Tornesit films. It has been determined, however, that, in general, most resins in Tornesit formulations accelerate checking of the film and appear to have no useful purpose beyond increasing the total solids of the paint.

A film formed from a simple toluene solution of Tornesit is brittle and has

<sup>a</sup> The addition of polyvinyl resins is said to increase the adhesive power and the fastness to light. G. Schultze, U. S. P. 1,980,959, Nov. 13, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 530. Nevinol is reported (E. R. Coyle, *Drugs, Oil and Paints*, Aug. 1935) to be a good plasticizer for chlorinated rubber coatings, e.g., Tornesit, imparting flexibility and resistance to water, alkalies and acids. The plasticizer is an oily, high-boiling polymer, apparently obtained from coal-tar naphtha.

<sup>b</sup> Also Dulux R. C. 119 & 120, Bakelite XR 4406, Rezyl 1103 and sulphurized aromatic hydrocarbons, French P. 784,471, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 6002. See Chapter 50, for a discussion of the last type of compound.

<sup>c</sup> A polystyrene resin.

<sup>d</sup> An alkylid resin.

•poor adhesion, although it has great chemical resistance. As outlined above, flexibility and adhesion can be obtained without sacrificing chemical resistance by proper selection of plasticizers from the list of compatible materials.

Unpigmented Tornesit films, like clear nitrocellulose lacquer, break down under direct outdoor exposure. A 100 per cent Tornesit film compared with a nitrocellulose-dammar film, by exposing both through glass to ultraviolet irradiation, showed that the discoloration of the Tornesit film was no greater than the nitrocellulose-dammar film. Clear films, however, serve many useful purposes indoors, because the chemical resistance of Tornesit is greater than most resins and pigments used in the compounding of paint.

The more important field for Tornesit is in pigmented products. A fairly wide range of pigments has been used in Tornesit films for outside and specialty paints. Those actually tested include zinc oxide, lithopone, Titanox, carbon black, bone pitch, oil black, chrome yellow, chrome green, Prussian blue, toluidine red and various grades of iron oxide and red lead. Of these, Prussian blue, chrome green, chrome yellow, red lead, and lithopone fade and discolor considerably. Bone pitch does not produce gas, as it does in nitrocellulose lacquers. Paints with these pigments have been exposed to weathering conditions for more than two years and results have shown excellent protection for the metal, and the films can be polished to a good surface. Coatings pigmented with toluidine red showed the least amount of fading and, in general, gave best results.

TABLE 58.—Paint Formulas using Tornesit.

1. GENERAL PRIMER (Good adhesion and flexibility)		5. CONCRETE PAINT (Good adhesion to concrete. Two coats recommended.)	
	Parts		Parts
Tornesit.....	20	Tornesit.....	20
Tung Oil <sup>96</sup> .....	6-10	Tung Oil.....	6-10
Hercolyn <sup>96</sup> .....	6	Hercolyn.....	6
Iron Oxide.....	15	Titanium Dioxide.....	12.75
Xylol.....	15	Carbon Black.....	0.25
Naphtha 54° Be.....	10	Xylol.....	15
Hiflash Solvent Naphtha.....	50	Naphtha 54° Be.....	10
		Hiflash Solvent Naphtha.....	50
2. ACID-RESISTANT FINISH		6. SALT-WATER-RESISTANT FINISH	
	Parts		Parts
Tornesit.....	20	Tornesit.....	20
Tung Oil.....	6-10	Refined Sardine Oil.....	10
Hercolyn.....	6	Indene Resin (M. P. 150°C.).....	8
Indian Red.....	15	Indian Red.....	15
Xylol.....	15	Xylol.....	15
Naphtha 54° Be.....	10	Naphtha 54° Be.....	10
Hiflash Solvent Naphtha.....	50	Hiflash Solvent Naphtha.....	50
3. ALKALI-RESISTANT FINISH		7. SPECIAL INTERIOR FINISH (For chlorine resistance and other severe interior uses apply two coats clear over general primer No. 1. Aging greatly benefits resistance.)	
	Parts		Parts
Tornesit.....	20	Tornesit.....	20
Hercolyn.....	13	Xylol.....	15
Indian Red.....	15	Naphtha 54° Be.....	10
Xylol.....	15	Hiflash Solvent Naphtha.....	50
Naphtha 54° Be.....	10		
Hiflash Solvent Naphtha.....	50		
4. ACID- AND ALKALI-RESISTANT FINISH (Sulpho-Terpoil discolors badly and is suitable only for dark colors.)			
	Parts		
Tornesit.....	20		
Sulphurized Terpene <sup>97</sup> .....	15		
Indian Red.....	15		
Xylol.....	15		
Naphtha 54° Be.....	10		
Hiflash Solvent Naphtha.....	50		

<sup>96</sup> The tung oil used here is Thermolysed Tung Oil No. 976. See the patents of F. M. Reese, to O'Brien Varnish Co.; in Chapter 61.

<sup>97</sup> Hydrogenated ethyl abietate.

<sup>98</sup> Sold under the name "Sulpho-Terpoil."



In Table 58 are some of the paint formulations in which Tornesit has been used satisfactorily. The general primer, which is given first, is employed as an undercoat for the various finishes which follow it in this table.

As indicated one of the most outstanding characteristics of Tornesit paints is their great resistance to corrosive influences.<sup>98</sup> Not only is usual protection afforded steel against rusting but, because of the chemical inertness of chlorinated rubber, Tornesit paints, when properly made, exhibit striking resistance to 50 per cent ammonium nitrate solution, 5-50 per cent sodium hydroxide, 5-70 per cent sulphuric acid, 85 per cent phosphoric acid, 10 per cent hydrochloric acid, 10 per cent nitric acid, organic acids, such as 5-80 per cent lactic, bleach solutions, and corrosive gases, such as chlorine, sulphur dioxide and ammonia.

The various properties of Tornesit as outlined above indicate a wide field of utility in protective coatings. These include non-inflammable smoke-, acid- and alkali-resistant paints for structural steel, ships and concrete. Among the other fields of application are the impregnation of fabric and paper, electrical insulation and the preparation of adhesives and plastic bodies.

Another item of interest is that concerning the electrical properties<sup>99</sup> of Tornesit films. Clear Tornesit has dielectric properties equal to or better than those of any other protective coating. Dielectric strength is retained even in the presence of moisture. Plasticized Tornesit films are also very efficient in this respect insofar as they have been tested. The lowering of the dielectric strength depends on the type and particle size of the pigment added, small particle size being most satisfactory.

The following are some of the values determined:

Power factor at 1000 cycles . . . . .	0.003
Dielectric strength (4 mil sheet) . . . . .	2300 volts per mil
Arcover test (discharge before breakdown) . . . . .	Good
Surface resistivity (24°C., 85% relative humidity) . . . . .	$2 \times 10^{13}$ ohms

Because of its corrosion-resistance chlorinated rubber has been used to coat iron pipes placed underground.<sup>100</sup> The resistance of chlorinated-rubber films to various reagents has been found satisfactory by many investigators.<sup>101</sup> Some, however, have not been so favorably impressed with the properties of chlorinated rubber.<sup>102</sup>

Rosenthal and Schultze,<sup>103</sup> who found that all samples of chlorinated rubber are not equally resistant, proposed two tests for the evaluation of these products. One involves heating a solution of the material to be tested in an oil bath at 100°C. and noting the time required for a strip of congo paper 5 cm. above the liquid to turn cornflower-blue. The other is more difficult to apply since it depends on

<sup>98</sup> After three years of exposure on a test fence in Wilmington, Delaware, steel panels coated with Tornesit paints were well protected, and the metal was still bright and free from rust under the paint. See also French P. 772,511, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1681.

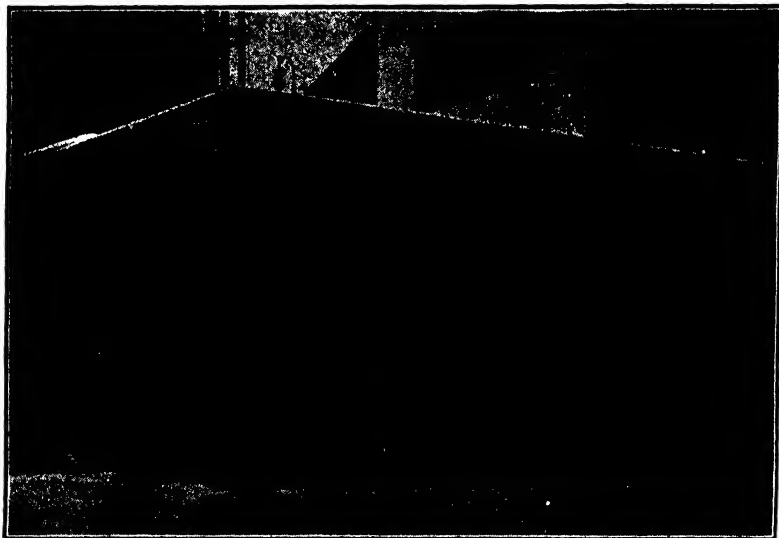
<sup>99</sup> Further electrical constants are given by R. Hasho, *J. Soc. Rubber Ind. Japan*, 1934, 7, 504; *Chem. Abs.*, 1935, 29, 954.

<sup>100</sup> Weckworth, *Gas- und Wasserfach*, 1932, 75, 69; *Chem. Abs.*, 1932, 26, 2558.  
<sup>101</sup> J. C. Fol and A. B. Bijl, *Chem. Weekblad*, 1932, 29, 162; *Bull. Rubber Growers' Assoc.*, 1932, 14, 310; *Chem. Abs.*, 1932, 26, 3958. R. Salzer, *Farbe u. Lack*, 1932, 452; *Chem. Abs.*, 1932, 26, 5775.  
<sup>102</sup> F. Rosendahl, *Chem.-Ztg.*, 1932, 56, 729; *Brit. Chem. Abs. B*, 1932, 1043. O. Mauermann, *Farbe u. Lack*, 1930, 390, 405; *Chem. Abs.*, 1930, 24, 5170; *Schweiz. Ver. Gas Wasserfach. Monats.-Bull.*, 1932, 12, 73; *Chem. Abs.*, 1932, 26, 4160; *Stahl u. Eisen*, 1930, 50, 985. O. Merz, *Farben-Ztg.*, 1933, 36, 1361; *Brit. Chem. Abs. B*, 1934, 30. K. Kojima and Y. Toyabe, *J. Soc. Chem. Ind. Japan*, 1933, 36, Suppl. binding, 236; *Chem. Abs.*, 1933, 27, 3852.

<sup>103</sup> See for instance W. Krumbhaar, (*Official Digest Federation Paint Varnish Prod. Clubs*, 1934, 133, 33; *Chem. Abs.*, 1934, 28, 2939. *Oil and Color Trades J.*, 1933, 63, 1464; *Chem. Abs.*, 1933, 27, 4953. *Chem. Industries*, 1933, 33, 506) and E. Karsten (*Kautschuk*, 1933, 9, 41; *Chem. Abs.*, 1933, 27, 4126). Replies to Krumbhaar have been made by F. C. Dvche-Teague (*Oil and Color Trades J.*, 1933, 1623). J. B. Serreston (*ibid.*), and C. A. Redfern (*Rubber Age*, 1933, 34, 113; *Chem. Abs.*, 1934, 28, 1889); they have found that chlorinated rubber is entirely satisfactory. Investigations carried out in the author's laboratory have shown that chlorinated rubber has excellent properties and is one of the best flexible resistant materials yet encountered.

<sup>104</sup> L. Rosenthal and G. Schultze, *Farben-Chem.*, 1934, 5, 53. Reviewed in *Synthetic and Applied Finishes*, June, 1934, 5, 65; *Chem. Abs.*, 1934, 28, 3618. See also Schultze, *Gas u. Wasserfach*, 1935, 78, 68; *Chem. Abs.*, 1935, 29, 2373.

having films of equal thickness. The test consists in measuring the degree to which a polished copper plate coated with the chlororubber turns dark when exposed to a mercury-arc. When paints are made from chlororubber of good stability and when properly pigmented and plasticized, these paints are durable and should find extensive application where protective coatings resistant to severe chemical, mechanical and atmospheric influences are required. Rosenthal and Schultze agreed with Krumbhaar<sup>104</sup> that the unpigmented films are sensitive to light. Gardner and Stewart<sup>105</sup> reported similar results with pigmented and clear varnishes. Another investigator noting differences existing between samples of



Courtesy Hercules Powder Company

FIG. 145.—Tornesit Paint Applied by Brushing on Exterior of Open-Top Tank Containing Hot Sulphuric Acid.

chlorinated rubber was Merz,<sup>106</sup> who found that the proportion of hot-water-soluble chlorine varied greatly.

It has already been stated that chlorinated rubber decomposes at about 150°C. Rinse<sup>107</sup> reported that, at 100°C., the loss of weight is still less than 5 per cent after 400 hours. The loss in weight from a film deposited by evaporation of a chloroform solution may be due to hydrochloric acid and residual chloroform.<sup>108</sup> The tendency to occlude traces of solvents has been noticed both by Rosenthal and Schultze<sup>109</sup> and by Jordan.<sup>110</sup> Because of this property, solvents boiling higher than xylene should not be used unless the coating is to be baked. Rosendahl<sup>111</sup> reported that no hydrogen chloride was evolved during exposure to ultraviolet light even after 17 days.

Mention has already been made of the fact that the use of various plasticizers is sometimes desirable to increase the flexibility and adhesion of chlorinated rubber

<sup>104</sup> W. Krumbhaar, *loc. cit.*

<sup>105</sup> H. A. Gardner and J. R. Stewart, *Circ., Am. Paint, Varnish Mfrs.' Assoc.*, 1932, 410, 164; *Chem. Abs.*, 1932, 26, 3940.

<sup>106</sup> O. Merz, *Kautschuk*, 1933, 9, 86; *Chem. Abs.*, 1933, 27, 4126.

<sup>107</sup> J. Rinse, *Chem. Weekblad*, 1932, 29, 521; *Brit. Chem. Abs. B*, 1932, 1093.

<sup>108</sup> J. G. Fol and A. B. Bijl, *Chem. Weekblad*, 1932, 29, 443; *Chem. Abs.*, 1932, 26, 6180.

<sup>109</sup> L. Rosenthal and G. Schultze, *loc. cit.*

<sup>110</sup> O. Jordan, "Chemische Technologie der Lösungsmittel," Springer, Berlin, 1932, 85.

<sup>111</sup> F. Rosendahl, *Chem.-Ztg.*, 1932, 56, 723; *Brit. Chem. Abs. B*, 1932, 1043.

films. Clear unpigmented films have at times a tendency to leave white spots on drying; this can be eliminated by the use of resins, camphor, triphenyl phosphate and trieresyl phosphate, which act as plasticizers.<sup>112</sup> Diethyl phthalate, pentachloroethane<sup>113</sup> and sulphonalkylamides of aromatic hydrocarbons<sup>114</sup> improve the flexibility. Since cumarone resin is not readily attacked by acids and alkalies, it may be added to increase the concentration of the coating solution without materially affecting the viscosity.<sup>115</sup> Such a mixed lacquer has been found to be particularly applicable as a coating for concrete.<sup>116</sup>

Other plasticizers which are stable to hydrolyzing agents are the chlorinated biphenyl compounds,<sup>117</sup> alkylated polynuclear aromatic hydrocarbons<sup>118</sup> and hydrogenated alkyl or aralkyl esters of abietic acid.<sup>119</sup> Phthalic acid esters when mixed with chlorinated rubber gave very hard surfaces and were highly resistant to the action of motor fuels.<sup>120</sup> Neutral suint and chlororubber have been proposed as a composition for the initial coating of porous objects before painting.<sup>121</sup> A transparent, waterproof material can be prepared from chlorinated rubber, a wax (paraffin, carnauba and montan wax) and dibutyl phthalate.<sup>122</sup>

Various drying oils have also been used as plasticizing agents, producing oil varnishes. In the customary method of making an oil varnish, the resin is melted to increase its solubility, hot oil is admixed, whereupon thinner is added. Since chlorinated rubber may decompose when heated to temperatures above 150°C., it is incorporated by mixing in solution with the oil, either cold or at a temperature not above 100°C., the solvent serving to replace part of the thinner otherwise required in the varnish.<sup>123</sup> The addition of chlorinated rubber decreases the permeability of a boiled linseed oil to sulphur dioxide, hydrogen chloride and ammonia.<sup>124</sup> When a small amount of linseed oil (1-3 per cent) is added a dull or flat finish is obtained.<sup>125</sup> Larger amounts of drying oils, for example from 40 per cent up to equal proportions based on the weight of dry chlorinated rubber, gave a varnish drying to a bright, glossy surface.<sup>126</sup>

To avoid turbid solutions of tung oil and chlorinated rubber that dry to frosted or dull films, Boehmer<sup>127</sup> suggested the selection of the two materials on the basis of the amount of chlorine combined with the rubber and the degree of polymerization of the oil. As the chlorine content of the rubber increased, the oil required more cooking in order that clear solutions might be obtained. A well-boiled oil, of course, dries more rapidly than raw oil and a highly chlorinated rubber is more

<sup>112</sup> Carleton Ellis, U. S. P. 1,541,693, June 9, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2277. See also French P. 748,494, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5561.

<sup>113</sup> Carleton Ellis, U. S. P. 1,750,563, March 11, 1930, to Chadeloid Chemical Co.; *Brit. Chem. Abs. B*, 1931, 77.

<sup>114</sup> N. Bennett, British P. 417,194, 1933, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1934, 1072.

<sup>115</sup> Carleton Ellis, U. S. P. 1,541,693, June 9, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2277.

<sup>116</sup> N. Boehmer, U. S. P. 1,572,065, Feb. 9, 1926, to Chadeloid Chemical Co.; *Chem. Abs.*, 1926, 20, 1331. For a further discussion concerning the use of chlororubber as a coating on concrete, see *Sci. Sect. Circ., Nat. Paint, Varnish, Lacquer Assoc., Inc.*, 1934, 471, 297; *Chem. Abs.*, 1935, 29, 363.

<sup>117</sup> W. Koch, U. S. P. 1,950,894, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 3620. See also L. Rosenthal and G. Schultze, *loc. cit.* A discussion of chlorinated biphenyl is found in Chapter 56.

<sup>118</sup> French P. 771,745, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1666. A paint which is reported to protect metals from sea water consists of chlorinated rubber, benzyl naphthalene, chlorinated biphenyl, chlorinated naphthalene, white lead, micaceous iron and solvent. French P. 775,061, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 2375.

<sup>119</sup> W. Koch, U. S. P. 1,957,786, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 4256. See also R. A. Coolahan, *loc. cit.*

<sup>120</sup> L. Rosenthal and G. Schultze, *loc. cit.*

<sup>121</sup> R. W. Moll, French P. 750,777, 1933; *Chem. Abs.*, 1934, 28, 1305.

<sup>122</sup> French P. 750,013, 1933, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 593.

<sup>123</sup> *Paint, Oil, Chem. Rev.*, 1927, 84 (5), 10.

<sup>124</sup> *Farben-Ztg.*, 1933, 38, 481; *Chem. Abs.*, 1933, 27, 1771.

<sup>125</sup> Carleton Ellis, U. S. P. 1,541,693, June 9, 1925, to Chadeloid Chemical Co.; *Chem. Abs.*, 1925, 19, 2277.

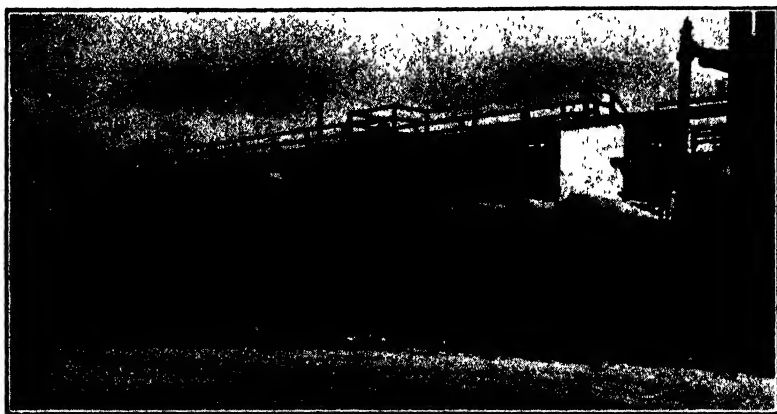
<sup>126</sup> Carleton Ellis, U. S. P. 1,695,840, Dec. 18, 1928, to Chadeloid Chemical Co.; *Chem. Abs.*, 1929, 23, 1000.

<sup>127</sup> N. Boehmer, U. S. P. 1,635,812, July 12, 1927, to Chadeloid Chemical Co.; *Chem. Abs.*, 1927, 21, 2992.

soluble than one of lower chlorination. Proper treatment of the two materials therefore results in a very satisfactory film.

A varnish of this type, yielding a smooth, glossy finish, was made up as follows: 25 parts of chlorinated rubber, containing approximately 67 per cent of combined chlorine, were dissolved in 50 parts of solvent naphtha and 75 parts of prepared tung oil. The latter was made by cooking the raw oil for 45 minutes at 200°C. with about 12 per cent of limed rosin. The mixture was then thinned with turpentine and solvent naphtha to the proper consistency and allowed to stand to precipitate foreign matter. Aliphatic hydrocarbons of the benzine type tend to decrease the solubility of chlorinated rubber and therefore could not be present in large proportions as thinners. A film of this material dried dust-free in 2 hours and was hard, tough, clear and glossy when thoroughly dry. The proportion of oil can be varied to meet particular needs and other drying oils may be added to the varnish.

The use of a smaller proportion of tung oil leads to the production of a quick-drying varnish.<sup>128</sup> Thus, highly chlorinated rubber, dissolved in toluene or solvent



*Courtesy Hercules Powder Company*

FIG. 146.—Four Cylindrical Tanks Protected against Sulphuric and Nitric Acid Fumes by Spraying with Tormesit Paint.

naphtha, was mixed with 10 per cent of its weight of tung oil to produce a composition that dried quickly to a clear, tough, non-inflammable film. This mixture could be employed for ordinary varnishing purposes, as well as for coating concrete or as an acid- and alkali-resistant varnish. Waxes (paraffin, ceresin or beeswax) incorporated in the solution gave a flatting varnish.

According to Geer,<sup>129</sup> vegetable oils (rapeseed, linseed, tung or corn oil) may be added to a solution of chlorinated rubber and the oil oxidized or vulcanized in the solution by sulphur chloride or by heating with sulphur. The material is useful as an acid- and alkali-resistant coating and as a covering for balloon fabrics. After hardening with heat it can be used as a substitute for celluloid and ebonite. In a coating composition described by Bradley and Gibbons,<sup>130</sup> chlorinated vulcanized rubber was dissolved in a mixture of a low-boiling and a high-boiling solvent (benzol and solvent naphtha) to give a low-viscosity varnish or paint. Such pigments as sublimed white lead, titanium oxide, ultramarine and toluidine toner were utilized to obtain colored enamels.

The color of solutions of chlorinated rubber may be improved by bleaching

<sup>128</sup> Carleton Ellis, U. S. P. 1,695,638, Dec. 18, 1928, to Chafeloid Chemical Co.; *Chem. Abs.*, 1929, 23, 999.

<sup>129</sup> W. C. Geer, U. S. P. 1,773,101, Aug. 19, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 5172.

<sup>130</sup> C. E. Bradley and W. A. Gibbons, U. S. P. 1,703,920, Mar. 5, 1929, to Naugatuck Chem. Co.; *Chem. Abs.*, 1929, 23, 2072.

with fuller's earth<sup>121</sup> or oil-soluble dyes may be added to give a colored lacquer.<sup>122</sup> Both the acidity and turbidity can be eliminated in chlorinated rubber paints by the use of quicklime, sodium carbonate or marble dust to neutralize the acid while calcium chloride can be employed to remove water.<sup>123</sup> Schmidt and Deseniss<sup>124</sup> mixed into the varnish of chlorinated rubber pulverized carborundum or quartz of grain size 40-100 microns. This improved the adherence to smooth surfaces and also the resistance to shock and abrasion.

Solutions of chlorinated rubber have been suggested for sealing bottles. The neck of the stoppered container is immersed into the solution a number of times until a film of sufficient thickness is formed; the chlororubber is then precipitated by dipping into alcohol and is dried.<sup>125</sup> Van Heuckeroth<sup>126</sup> stated that a solution of chlorinated rubber is a satisfactory vehicle for calcium sulphide in luminous paints.

### MOLDINGS

Some of the earliest investigators in the field, for example Engelhard, Havemann and Day,<sup>127</sup> proposed that dry chlorinated rubber be used as a molding compound. This was one of the uses which Dyche-Teague<sup>128</sup> also suggested for chlorinated rubber. Ostromislensky<sup>129</sup> mixed crude rubber on a rubber mill with chlorinated or brominated rubber in the proportion of 7-85 parts of the halogen-treated rubber to 10 parts of crude rubber. Heating the mixture in a press was stated to "vulcanize" it to an ebonite-like mass.

Latex can be utilized in making a molding composition. Halogens or halogen acids normally tend to coagulate latex and unless steps are taken to prevent the formation of a solid mass the batch cannot be readily chlorinated. The procedure is as follows: 100 parts of kieselguhr were moistened with 150 parts of water to which had been added 9 parts of concentrated ammonium hydroxide (to prevent coagulation of the latex subsequently used). Then 100 parts of latex, containing 36 per cent of solids, were added and the mixture stirred until homogeneous. Excess water was removed and the dried mass was subjected to the action of chlorine gas until no more was absorbed. Hydrogen chloride formed during the reaction was neutralized with ammonia and the material was washed and dried. The product could then be molded by pressing for 10 minutes at 115°C. forming a hard material which could be polished to a high luster. It was not affected by water, oils or gasoline.<sup>130</sup>

A thermoplastic molding compound may be obtained by mixing chlorinated rubber with a phenol-aldehyde condensation product.<sup>131</sup> A solution containing 1 part of rubber was treated with chlorine until the rubber had absorbed twice its weight of chlorine. To this solution were added 2 parts of phenol and 2 parts of a 40 per cent solution

<sup>121</sup> Carleton Ellis, U. S. P. 1,750,593, March 11, 1930, to Chadeloid Chemical Co.; *Brit. Chem. Abs.* B, 1931, 77.

<sup>122</sup> Carleton Ellis, U. S. P. 1,695,639, Dec. 18, 1928, to Chadeloid Chemical Co.; *Chem. Abs.*, 1929, 23, 997.

<sup>123</sup> N. Boehmer, U. S. P. 1,807,616, June 2, 1931; *Chem. Abs.*, 1931, 25, 4443.

<sup>124</sup> A. Schmidt and M. Deseniss, U. S. P. 1,950,820, March 13, 1934, to Deutsche Tornesit-Ges.m.b.H.; *Chem. Abs.*, 1934, 28, 3605. British P. 355,547, 1930, to New-York Hamburger Gumm-Waaren Compagnie; *Chem. Abs.*, 1932, 26, 4207. French P. 714,808, 1931; *Chem. Abs.*, 1932, 26, 1684.

<sup>125</sup> A. Lambie, British U. 141,220, 1919, to United Alkali Co.; *Chem. Abs.*, 1920, 14, 2566.

<sup>126</sup> A. W. Van Heuckeroth, *Circ. Amer. Paint, Varnish Mfrs.' Assoc.*, 1933, 440, 327; *Brit. Chem. Abs.* B, 1933, 1068.

<sup>127</sup> G. A. Engelhard and R. F. Havemann, U. S. P. 26,175, Nov. 22, 1859. G. A. Engelhard and H. H. Day, British P. 2734, 1859.

<sup>128</sup> F. C. Dyche-Teague, U. S. P. 1,819,136, Aug. 18, 1931; *Chem. Abs.*, 1931, 25, 677. British P. 305,908, 1927; *Brit. Chem. Abs.* B, 1929, 834.

<sup>129</sup> I. I. Ostromislensky, U. S. P. 1,342,586, Oct. 9, 1917; *Chem. Abs.*, 1918, 12, 256. *J. Russ. Phys.-Chem. Soc.*, 1915, 47, 1898; 1916, 48, 1114; *Chem. Abs.*, 1916, 10, 1945; 1917, 11, 1766.

<sup>130</sup> E. Hopkinson, U. S. P. 1,491,265, April 22, 1924; *Chem. Abs.*, 1924, 18, 2266. Canadian P. 250,476, 1925; *Chem. Abs.*, 1925, 19, 3287. British P. 201,898, 1922, to Naugatuck Chemical Co.; *J.S.C.I.*, 1924, 43, 918B.

<sup>131</sup> J. McGavack, U. S. P. 1,555,131, Sept. 29, 1925, to Revere Rubber Co.; *Chem. Abs.*, 1925, 19, 3617. British P. 233,873, 1924; *J.S.C.I.*, 1925, 44, 463B. See also D. F. Twiss and J. A. Wilson, British P. 417,373, 1934, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1935, 29, 1177. French P. 773,621, 1934, to Soc. Anon. des pneumatiques Dunlop; *Chem. Abs.*, 1935, 29, 1535.

of formaldehyde and the mixture was boiled under reflux for 2 hours. The material was washed with hot water, worked on a cold rubber mill to expel water, then ground and dried. The dry powder was thermoplastic and could be molded at a pressure of 3000-4000 pounds per square inch at a temperature of 175°C. The molded article was hard, opaque and would receive a bright finish from a polished mold. It was insoluble in acids and alkalies and resistant to electrical currents. Chlorinated vulcanized rubber could be substituted for chlororubber,<sup>142</sup> and the resulting composition used for bonding abrasive materials.<sup>143</sup> A similar reaction product between phenol and chlorinated rubber has been recommended for painting ship bottoms.<sup>144</sup>

A water-resistant insulating material was made by Plauson<sup>145</sup> by adding urea to fused chlorinated rubber and treating the mixture with formaldehyde. Its properties could be varied by the addition of natural resins or resin oils.

Chlorinated rubber, after softening to the form of a gel with carbon disulphide, can be extruded to form a silk-like fiber.<sup>146</sup> The solvent is removed by evaporation or by leading the extruded fiber into alcohol, acetic acid or gasoline. Plasticizers make the fiber more flexible. The thread has a fair luster, is noninflammable and can be woven into a web or fabric. Colored fibers are obtained by adding a dye to the gelled mass.

#### MISCELLANEOUS OTHER USES OF HALOGENATED RUBBER

The properties of halogenated rubber have suggested several other uses. For instance, since it only chars and does not burn when held in the flame it has been proposed as a fire-retarding insulator.<sup>147</sup> Deseniss and Nielsen<sup>148</sup> mixed chlorinated rubber with tar, asphalt and other bituminous substances and employed the resulting product as an insulator on metal pipe. Finely ground asbestos may also be added to such a mixture. Chlorinated rubber has even been advocated as an addition to the bituminous materials used in road construction.<sup>149</sup>

Warner<sup>150</sup> made an adhesive from brominated rubber for uniting rubber to metal. A solution of chlorinated rubber has been described as an adhesive for paraffined paper.<sup>151</sup> When these solutions of chlorinated rubber contain a large proportion of solids, they can be used as cements.<sup>152</sup> The flexibility of such cements is increased by the addition of softeners such as camphor, triphenyl and tricresyl phosphates, or semi-drying oils, e.g., corn or peanut oil.<sup>153</sup> Incorporation of extending agents is useful in overcoming shrinkage. Examples of agents of this type are whiting, zinc oxide, barytes, litharge, silex, asbestos, talc and organic materials such as cotton wool and wood flour.

<sup>142</sup> J. McGavack, U. S. P. 1,640,364, Aug. 30, 1927, to Revere Rubber Co.; *Brit. Chem. Abs. B*, 1927, 885.

<sup>143</sup> R. C. Benner and G. H. Porter, U. S. P. 1,825,771, Oct. 6, 1931, to Carborundum Co.; *Brit. Chem. Abs. B*, 1932, 726.

<sup>144</sup> K. Morimoto, Japanese P. 90,520, 1931; *Chem. Abs.*, 1931, 25, 4723. See also H. L. Fisher, U. S. P. 1,890,903, Dec. 13, 1932, to B. F. Goodrich Co.; *Chem. Abs.*, 1933, 27, 2001.

<sup>145</sup> H. Plauson, German P. 550,260, 1931; *Chem. Abs.*, 1933, 27, 1220.

<sup>146</sup> Carleton Ellis, U. S. P. 1,544,529, June 30, 1925, to Chadeloid Chemical Co. U. S. P. 1,695,643, Dec. 18, 1928; *Chem. Abs.*, 1929, 23, 1013.

<sup>147</sup> T. A. Edison, U. S. P. 438,309, Oct. 14, 1890. For the use of chlorinated rubber in making insulating paper, see *Gummi-Ztg.*, 1922, 1266; *Kunststoffe*, 1922, 12, 166.

<sup>148</sup> M. Deseniss and A. Nielsen, U. S. P. 1,890,723, Dec. 13, 1932, to New-York Hamburger Gummi-Waaren Compagnie; *Chem. Abs.*, 1933, 27, 1688. French P. 714,805, 1931; *Chem. Abs.*, 1932, 26, 1634; British P. 353,311, 1930; *Brit. Chem. Abs. B*, 1931, 936.

<sup>149</sup> French P. 754,119, 1933, to Soc. J. R. Geigy S. A.; *Chem. Abs.*, 1934, 28, 1165. British P. 411,640, 1934; *Chem. Abs.*, 1934, 28, 6973.

<sup>150</sup> R. M. Warner, U. S. P. 1,869,636 and 1,869,638, Aug. 2, 1932, to Miller Rubber Co.; *Chem. Abs.*, 1932, 26, 5452.

<sup>151</sup> French P. 753,542, 1933, to N. V. de Bataafsche Petroleum Maatschappij; *Chem. Abs.*, 1934, 28, 1155.

<sup>152</sup> Carleton Ellis, U. S. P. 1,695,637, Dec. 18, 1928, to Chadeloid Chemical Co.; *Chem. Abs.*, 1929, 23, 1013.

<sup>153</sup> Safety glass is one of the suggested applications of such cements. W. D. Spencer, British P. 414,073, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 569.

Cottonseed oil, which has been treated with chlorine at an elevated temperature until the oil has increased 30 per cent in weight, is a solvent for chlorinated rubber. When this oil is added to a solution of chlorinated rubber in carbon tetrachloride and the latter evaporated, the product is stated to be a coating material for fly paper<sup>154</sup> or may be added to varnishes to improve their elasticity.<sup>155</sup> Chlorinated drying and semi-drying oils have also been employed with chlororubber in rubber compositions.<sup>156</sup>

Ellis<sup>157</sup> impregnated or coated fabrics and paper with chlorinated rubber to make them fire-resistant,<sup>158</sup> a property depending to some extent on the degree of chlorination and the thickness of the coating. Such coatings are also waterproof



Courtesy Hercules Powder Company

FIG. 147.—Comparison Test of Tornesit (right) on Cooling Coils Subjected to Moisture and Acid Fumes.

and may be made more flexible by the addition of softening agents. Deseniss<sup>159</sup> stated paper coated with a thin solution of chlorinated rubber is made more durable for stencil and copying purposes. Stevens and Gaunt<sup>160</sup> report that chlorinated rubber in benzene gives a satisfactory showerproof coating.

Preparations for coating or impregnating various materials are made by form-

<sup>154</sup> C. Thieme, U. S. P. 1,527,715, Feb. 24, 1925; *J.S.C.I.*, 1925, 44, 291B. German P. 375,290, 1921; *J.S.C.I.*, 1924, 43, 64B.

<sup>155</sup> C. Thieme, German P. 364,831, 1920; *J.S.C.I.*, 1923, 42, 279A.

<sup>156</sup> D. F. Twiss, A. S. Carpenter and A. E. T. Neale, British P. 420,116, 1933, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs. B*, 1935, 114.

<sup>157</sup> Carleton Ellis, U. S. P. 1,852,998, April 5, 1932, to Chadeloid Chemical Co.; *Chem. Abs.*, 1932, 26, 3122. For a review on the use of chlororubber in the textile industry, see *Silk and Rayon*, 1934, 8, 305; *Brit. Chem. Abs. B*, 1935, 34.

<sup>158</sup> Cf. the preparation of fireproof fabrics by successive impregnations with metallic salts and chlororubber, M. Leatherman, U. S. P. 1,961,108, May 29, 1934, and 1,990,292, Feb. 5, 1935, to free use of the public; *Chem. Abs.*, 1934, 28, 4597; 1935, 29, 1934.

<sup>159</sup> M. Deseniss, U. S. P. 1,823,260, Sept. 15, 1931, to A. Feurich; *Chem. Abs.*, 1932, 26, 268.

<sup>160</sup> H. P. Stevens and R. Gaunt, *Bull. Rubber Growers' Assoc.*, 1933, 15, 658; *Chem. Abs.*, 1934, 28, 2568. Cf. the waterproofing of photographic paper, J. Holden, British P. 418,976, 1933, to J. Halden and Co., Ltd.; *Brit. Chem. Abs. B*, 1935, 135.

ing aqueous emulsions of chlorinated rubber dissolved in organic solvents or mixed with drying oils.<sup>161</sup>

Chlorinated rubber may also be applied in preparing paper filter packs for edge filtration,<sup>162</sup> in treating airplane wings<sup>163</sup> or rubber-impregnated filter cloths,<sup>164</sup> in printing designs on raw pasteboard,<sup>165</sup> and in manufacturing artificial leather by binding together comminuted cork and fibers.<sup>166</sup>

Since halogenated rubber is adequately resistant to oxidation and does not swell in the presence of water and many solvents it has found use as a facing or lining material. Arnold<sup>167</sup> made a printer's blanket which had a top layer of chlorinated rubber. Garvey<sup>168</sup> protected soft vulcanized rubber with a coat of chlorinated rubber. The method suggested was to subject the rubber to the action of chlorine and then to apply a solution of chlorinated rubber and o-nitrodiphenyl ether. The surface of rubber-covered cloth is made hard and smooth by treatment with a heavy metal salt of a fatty acid, followed by halogenation.<sup>169</sup> Twiss and Jones<sup>170</sup> hardened the surface of golf balls by the action of chlorine. Bales of rubber were protected from oxidation through bromination of their surfaces.<sup>171</sup> Further applications of chlororubber include uses as a stuffing for pillows,<sup>172</sup> as an ingredient in chewing gum<sup>173</sup> and to assist in the hot cure of Thiokol.<sup>174</sup>

Chlorinated gutta-percha solutions are less viscous than those of chlorinated rubber of corresponding concentration. They can be used as lacquers and form bright, hard, though somewhat brittle films. The brittleness may be modified by the addition of softeners, and natural and synthetic resins may also be added. Ellis reported that the films offer excellent resistance to the action of acids and alkalis.<sup>175</sup>

<sup>161</sup> French P. 745,229, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4441. British P. 409,009, 1932; *Brit. Chem. Abs.* B, 1934, 593. See also C. W. Richards and H. Dodd, British P. 414,072, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 251. Cf. British P. 412,525, 1934, to Chem. Fabr. Buckau; *Chem. Abs.*, 1935, 29, 641. French P. 769,342, 1934; *Chem. Abs.*, 1935, 29, 641.

<sup>162</sup> H. S. Hele-Shaw and J. A. Pickard, U. S. P. 1,744,510, Jan. 21, 1930; *Chem. Abs.*, 1930, 24, 1253. British P. 249,202, 1924; *Brit. Chem. Abs.* B, 1925, 423. Canadian P. 281,702, 1928; *Chem. Abs.*, 1928, 22, 4248. German P. 499,656, 1925; *Chem. Abs.*, 1930, 24, 4428.

<sup>163</sup> French P. 756,948, 1933, to Soc. des vernis perl.; *Chem. Abs.*, 1934, 28, 3555.

<sup>164</sup> L. Sylvain, M. Lejeune, and J. E. C. Bongrand, French P. 741,179, 1931; *Chem. Abs.*, 1933, 27, 2605. British P. 411,887, 1932; *Brit. Chem. Abs.* B, 1934, 754.

<sup>165</sup> British P. 418,467, 1934, to International Latex Processes, Ltd.; *Chem. Abs.*, 1935, 29, 2264.

<sup>166</sup> British P. 399,856, 1933, to Behr-Manning Corp.; *Chem. Abs.*, 1934, 28, 1823. See also S. J. Peachey, U. S. P. 1,234,381, July 24, 1917; *Chem. Abs.*, 1917, 11, 2626. British P. 1894, 1915; *J.S.C.I.*, 1916, 35, 479. Cf. E. Fröhlich, French P. 774,120, 1934; *Chem. Abs.*, 1935, 29, 3263.

<sup>167</sup> F. G. Arnold, U. S. P. 1,971,439, Aug. 28, 1934, to Rapid Roller Co.; *Chem. Abs.*, 1934, 28, 6538.

<sup>168</sup> B. S. Garvey, U. S. P. 1,810,560, June 16, 1931, to B. F. Goodrich Co.; *Chem. Abs.*, 1931, 25, 4741.

<sup>169</sup> French P. 759,270, 1934, to International Latex Processes, Ltd.; *Chem. Abs.*, 1934, 28, 3249. British P. 407,224, 1933; *Brit. Chem. Abs.* B, 1934, 400.

<sup>170</sup> D. F. Twiss and F. A. Jones, British P. 403,726, 1932, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs.* B, 1934, 213. French P. 770,928, 1934, to Soc. anon. des pneumatiques Dunlop; *Chem. Abs.*, 1935, 29, 959. See also D. F. Twiss, F. A. Jones and E. W. Allen, British P. 409,434, 1934, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1934, 28, 6260. D. F. Twiss, F. A. Jones and D. J. Hadley, British P. 415,195, 1934, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1935, 29, 958.

<sup>171</sup> E. Hopkinson, U. S. P. 1,442,218, Jan. 16, 1923; *Chem. Abs.*, 1923, 17, 1351.

<sup>172</sup> S. B. Cormack, British P. 415,795, 1934, to Imperial Chem. Ind. Ltd.; *Chem. Abs.*, 1935, 29, 1283.

<sup>173</sup> W. O. Snelling, U. S. P. 1,288,723, Dec. 24, 1918; *Chem. Abs.*, 1919, 13, 676.

<sup>174</sup> J. C. Patrick, U. S. P. 1,962,460, June 12, 1934; *Chem. Abs.*, 1934, 28, 4848. In Chapter 58, a further discussion of Thiokol is found.

<sup>175</sup> Carleton Ellis, U. S. P. 1,695,642, Dec. 18, 1928, to Chadeloid Chemical Co.; *Chem. Abs.*, 1929, 23, 999.



## Chapter 56

### Resins from Halogenated Compounds

There are two large classes of resins produced from halogenated compounds. The first class includes high-molecular-weight substances resulting from inter-molecular condensations with the elimination of halogen or hydrogen halide. The second class consists of the halogenated products which owe their amorphous and resinous properties to the fact that they are mixtures of several individuals, as for example, the chlorinated biphenyls and naphthalenes. These two classes of resins will be taken up in order.

#### CLASS I. CONDENSATION RESINS

Resin-like substances are formed by treating compounds of the type of benzyl chloride, benzal chloride, xylene dichloride, benzotrichloride or the naphthalene chlorides with metal halides (Friedel-Crafts reaction), with metals such as zinc, copper or nickel (Zincke reaction), or by the action of alkali metals on poly-halogenated hydrocarbons (Würtz-Fittig synthesis). In general such resins do not contain chlorine (or other halogens), as it is eliminated in the resin-forming reaction.

**Aralkyl-Halide Resins.** The Friedel-Crafts reaction is a fruitful source of tars and resins which are often the chief product in the case of a polyfunctional reactant like benzyl chloride which contains an aromatic nucleus and an alkyl halide residue in the same molecule. Böeseke<sup>1</sup> declares that this compound is not suitable for use in the Friedel-Crafts reaction if products of a definite composition are desired. On adding aluminum chloride to benzyl chloride, hydrogen chloride is evolved and a complex mixture of hydrocarbon polymers formed, the major portion of which are insoluble in all solvents.<sup>2</sup> The polymers have the empirical formula  $(C_7H_6)_n$ , and probably consist of macromolecules<sup>3</sup> made up of the group  $-C_6H_4CH_2-$ .<sup>4</sup>

Ferric chloride acting on benzyl chloride in the cold transforms the latter into a soluble, chlorine-free resin.<sup>5</sup> To 100 parts of benzyl chloride, 0.5 part of anhydrous ferric chloride is added while the mixture is stirred. Soon a vigorous evolution of hydrochloric acid begins and progresses regularly for a considerable period. The temperature increases only slightly. A dark brown, porous solid is formed, which is blown with steam to separate any unchanged benzyl chloride

<sup>1</sup> J. Böeseke, *Rec. trav. chim.*, 1904, 23, 98; *J.C.S.*, 1904, 86 (1), 384.

<sup>2</sup> W. H. Perkin and W. R. Hodgkinson, *J.C.S.*, 1880, 37, 721. C. Friedel and J. M. Crafts, *Bull. soc. chim.*, 1885, 43, 53. J. Schramm, *Ber.*, 1893, 26, 1706; *J.C.S.*, 1893, 64 (1), 561.

<sup>3</sup> It is possible that each molecule contains a chlorine atom at the end of the chain but in large molecules of this nature the percentage of chlorine would be very low and could not be determined accurately on account of the difficulty of purification. That chlorine is probably present is borne out by the work of E. Wertyporoch and A. Farnik (*Ann.*, 1931, 491, 265; *Chem. Abs.*, 1932, 26, 1275) who treated benzyl chloride in nitrobenzene solution with aluminum chloride at  $-15^\circ C$ . and isolated o- and p-chloromethyldiphenylmethane,  $C_6H_4CH_2-C_6H_4CH_2Cl$ , which can be considered the initial stage in the formation of the polymeric chain.

<sup>4</sup> R. A. Jacobson, *J.A.C.S.*, 1932, 54, 1513. Böeseke (*loc. cit.*) considered the fundamental group to be  $C_6H_4CH_2-$ .

<sup>5</sup> German P. 280,595, 1913, to Badische Anilin- & Soda-fabrik; *J.S.C.I.*, 1915, 34, 500.

and is then ground and washed with hydrochloric acid to remove ferric chloride. A yellowish resin is obtained, soluble in benzene, carbon tetrachloride, chloroform, cyclohexanone, cyclohexanol acetate and various other vehicles but insoluble in aliphatic alcohols, ketones and hydrocarbons. Solutions of the resin may be used for varnishing, and the coatings are resistant to acids and alkalis. Warm caustic soda solution of 35 per cent concentration does not attack the film.\* Ushakov and Kon' believe that benzyl-chloride resin will find industrial applications as a shellac substitute. According to Jacobson,<sup>8</sup> the resin is not compatible with nitrocellulose, cellulose acetate, polyvinyl acetate, polyvinyl chloride, drying oils or alkyd resins.

Zirconium tetrachloride has been suggested as a condensing agent for benzyl chloride in carbon disulphide solution to give a resin applicable as a shellac substitute. The resin thus prepared may be mixed with other resins, rubber, or gutta-percha.<sup>9</sup>

To summarize the effect of different catalysts in the condensation of benzyl chloride, it may be noted that polymerization in the presence of aluminum chloride furnishes an insoluble hydrocarbon polymer,  $(C_7H_8)_n$ , and a small amount of a soluble resin of the same empirical formula. If ferric chloride is used the yield of soluble resin increases at the expense of the insoluble polymer. With stannic chloride only the soluble resin is formed.<sup>10</sup> Jacobson found the molecular weight of the soluble resins to be about 2000. The insoluble polymers presumably have much higher molecular weights.

A mixture of  $\alpha$ - and  $\beta$ -chloromethylnaphthalene, dissolved in carbon bisulphide and treated with aluminum chloride, yields an elastic, brown, rubber-like substance insoluble in benzene. When  $\beta$ -chloromethylnaphthalene alone is employed very little resin is formed.<sup>11</sup>

Phenylethyl chloride is condensed by the action of aluminum chloride to a chlorine-free, tough, reddish mass, insoluble in most solvents.<sup>12</sup> This product may be represented as made up of the group  $-C_6H_5-CH_2CH_2-$ .

Zincke<sup>13</sup> permitted copper, silver and other metals to react on benzyl chloride. Onufrowicz,<sup>14</sup> who also studied the reaction between benzyl chloride and copper, obtained a resin when he heated the mixture in a sealed glass tube at a temperature of 150-160°C. When equal quantities of benzyl chloride and copper were heated (at this same temperature) for two hours in an open vessel, evolution of hydrogen chloride occurred accompanied by the formation of a thick liquid boiling between 110-360°C. and a tough resinous mass. The latter was soluble in benzene but only slightly so in alcohol. Evaporation of a benzene solution of the resin yielded a tough, yellow fluorescent body. At lower temperatures (100-140°C.) and in an atmosphere of dry carbon dioxide, hydrogen chloride was given off at 107°C. and only a liquid product secured.

According to Gladstone and Tribe,<sup>15</sup> a zinc-copper couple converts benzyl bromide into a resinous mass which is partly soluble in ether or benzene. The ether-soluble portion is a brittle, transparent, yellowish red resin melting at 42°C. Analogous results were obtained with benzyl chloride.

Prost<sup>16</sup> found that upon mixing zinc dust and benzyl chloride below the boiling

\* German P. 280,377, 1913, to Badische Anilin- & Sodafabrik; *J.S.C.I.*, 1915, 34, 500.

<sup>7</sup> S. N. Ushakov and A. V. Kon, *Zhur. Priklad. Khimii*, 1930, 3, 69; *Chem. Abs.*, 1930, 24, 3796.

<sup>8</sup> R. A. Jacobson, *loc. cit.*

<sup>9</sup> P. Krishnamurthy, British P. 298,939, 1927; *Chem. Abs.*, 1929, 23, 3114.

<sup>10</sup> R. A. Jacobson, *loc. cit.*

<sup>11</sup> E. Clar and L. Lombardi, *Gazz. chim. ital.*, 1932, 62, 559; *Chem. Abs.*, 1933, 27, 81.

<sup>12</sup> J. von Braun and H. Deutach, *Ber.*, 1913, 45, 1267; *Chem. Abs.*, 1913, 6, 2605.

<sup>13</sup> T. Zincke, *Ber.*, 1899, 2, 737; *Chem. Zentr.*, 1870, 66.

<sup>14</sup> A. Onufrowicz, *Ber.*, 1884, 17, 533; *J.C.S.*, 1884, 46, 1133.

<sup>15</sup> J. H. Gladstone and A. Tribe, *J.C.S.*, 1884, 47, 448.

<sup>16</sup> E. Prost, *Bull. soc. chim.*, 1898, 46, 247; *Chem. Zentr.*, 1896, 317.

point of the benzyl chloride he obtained a viscous product which could be distilled up to 340°C. From the distillate he isolated benzyl chloride, bibenzyl and toluene. The material boiling above 340°C. contained anthracene and a substance which appeared to be identical with the hydrocarbon  $C_{20}H_{18}$  found by Weber and Zincke.<sup>17</sup> At higher reaction temperatures, the result was a hard brown substance.

On heating benzyl chloride in a benzene solution with aluminum chips, Radziewanowski<sup>18</sup> observed that in addition to diphenylmethane, a large quantity of tarry material was formed. Nickel at a high temperature causes formation of the insoluble polymer of benzyl chloride.<sup>19</sup> Mailhe<sup>20</sup> obtained a yellow, voluminous mass on passing benzyl chloride vapor and hydrogen over hot nickel. Boiling benzyl chloride and magnesium react, according to Schorigin, Issagulianz and Gusseva, to give a glassy mass.<sup>21</sup>

Besides metals and metal chlorides, other catalysts have been suggested. Freund and Jordan utilized various surface catalysts, e.g., hydrated aluminum or magnesium silicates, kaolin, fuller's earth or silica.<sup>22</sup> In the attempt to improve the yield of monoalkyl ether of xylylene glycol, Quelet<sup>23</sup> heated 1',4'-dichlorodimethylbenzene with potassium hydroxide in dilute alcohol. An insoluble, yellow, condensation product resulted. A similar by-product is obtained in the preparation of 1',4'-dicyanodimethylbenzene from the corresponding dibromo derivative.<sup>24</sup>

**Aralkyl Halides and Hydrocarbons.** Although, as shown above, benzyl chloride forms resins of high molecular weight which may be either soluble or insoluble depending upon the extent of reaction and the particular catalyst, the inclusion of phenols or aromatic hydrocarbons such as naphthalene, anthracene, phenanthrene and various other coal-tar hydrocarbons, leads to soluble substances of relatively low molecular weight. The effect of these added substances is to limit the growth of the molecule so that it does not attain such a size that the product is insoluble. One example of this is the reaction of benzyl chloride with benzene in the presence of thallium trichloride and ferric chloride. The first was studied by Stadnikov and Kashtanov<sup>25</sup> who isolated diphenylmethane and p-benzylidiphenylmethane. The second was studied by Wertyporoch, Kowalski and Roeske,<sup>26</sup> who obtained triphenylmethane, two oils and a resin, in addition to diphenylmethane.

Condensation of benzyl chloride with methylnaphthalene in the presence of iron yields an odorless oil.<sup>27</sup> Impregnating agents, coatings and plastic insulating masses have been prepared from the condensation products of aralkyl halides on tar oil or its constituents.<sup>28</sup> An oil also was obtained when xylyl chloride and naphthalene were heated in an iron kettle for several hours at 100°C. Although the reaction has been stated to occur when the aralkyl halide and polynuclear hydrocarbon are heated together in absence of a catalyst,<sup>29</sup> Ushakov and Kon<sup>30</sup>

<sup>17</sup> E. Weber and T. Zincke, *Ber.*, 1874, 7, 1153; *Chem. Zentr.*, 1874, 675.

<sup>18</sup> C. Radziewanowski, *Ber.*, 1895, 28, 1135; 1894, 27, 3237; *J.C.S.*, 1895, 68 (1), 412, 129.

<sup>19</sup> A. Korczynski, A. Reinholz and E. Schmidt, *Roczniki Chem.*, 1929, 9, 731; *Chem. Abs.*, 1930, 24, 1858.

<sup>20</sup> A. Mailhe, *Chem.-Ztg.*, 1905, 29, 462; *Chem. Zentr.*, 1905, 1, 1555.

<sup>21</sup> P. Schorigin, V. Issagulianz and A. Gusseva, *Ber.*, 1933, 66, 1426; *Brit. Chem. Abs. A*, 1933, 1150.

<sup>22</sup> E. Freund and H. Jordan, German P. 417,667, 1921, to Chem. Fabr. auf Actien vorm. E. Schering; *Brit. Chem. Abs. B*, 1926, 100.

<sup>23</sup> R. Quelet, *Compt. rend.*, 1931, 192, 1391; *Chem. Abs.*, 1931, 25, 4539.

<sup>24</sup> A. F. Titley, *J.C.S.*, 1926, 515.

<sup>25</sup> G. L. Stadnikov and L. I. Kashtanov, *J. Russ. Phys.-Chem. Soc., Chem. Pt.*, 1928, 60, 1117; *Chem. Abs.*, 1929, 23, 2170. L. I. Kashtanov, *J. Gen. Chem. (U. S. S. R.)*, 1932, 2, 515; *Chem. Abs.*, 1933, 27, 975.

<sup>26</sup> E. Wertyporoch, I. Kowalski and A. Roeske, *Ber.*, 1933, 66, 1332; *Chem. Abs.*, 1934, 28, 1026.

<sup>27</sup> German P. 301,713, 1916, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1921, 40, 210A.

<sup>28</sup> German P. 301,713, 1916, and 302,531, 1917, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1921, 40, 210A, 344A. Austrian P. 88,133, 1917; *Chem. Zentr.*, 1926, 4, 930. See also German P. 336,476, 1918; *J.S.C.I.*, 1921, 40, 377A.

<sup>29</sup> German P. 416,904, 1920, to Farb. vorm. Meister, Lucius & Brüning; *Brit. Chem. Abs. B*, 1926, 100.

<sup>30</sup> S. N. Ushakov and A. V. Kon, *loc. cit.*

maintain that catalysts are indispensable since they failed to detect any reaction in their absence. Marschall<sup>31</sup> found that the presence of gaseous hydrogen chloride caused reaction to proceed at a low temperature.

Passing air through a suspension of manganese dioxide or ferric chloride in the oily condensation products from aralkyl halides and aromatic hydrocarbons produces harder materials.<sup>32</sup> A similar result is obtained by treating the oils with formaldehyde in conjunction with zinc chloride.<sup>33</sup> These hardened resins are readily soluble in aromatic hydrocarbons and linseed oil. Also they are stable towards light and resistant to water and alkalies. Other synthetic resins (phenol-formaldehyde, phenol-sulphur chloride and cumarone) may be hardened and made more soluble in hydrocarbons and linseed oil by treatment with benzyl chloride in presence of aqueous alkalies.<sup>34</sup>

A water-soluble condensation product is obtained by heating benzyl chloride with a solution of naphthalene sulphonic acid in sulphuric acid. Alternatively, a simple benzyl-halide-naphthalene resin may be prepared and then sulphonated with chlorosulphonic acid or oleum. Dichlorodihydronaphthalene can be used instead of benzyl chloride.<sup>35</sup>

Aralkyl chlorides also may be condensed with partly hydrogenated aromatic hydrocarbons. Dihydronaphthalene and dimethylbenzyl chloride heated to 200°C. (with a small proportion of zinc), or rosin and isopropylbenzyl chloride heated under reflux with ferric chloride, form resins which are soluble in linseed oil and in aliphatic hydrocarbons, but insoluble in alcohols.<sup>36</sup> Diphenylchloromethane and thiophene are condensed by the action of stannic chloride and form a resinous mass.<sup>37</sup>

Kränzlein and Voss made neutral resins by esterifying the condensation products initially formed from resins and aralkyl halides.<sup>38</sup> For example, 160 parts of colophony were mixed with 40 parts of benzyl chloride and warmed slowly. A little above 100°C. the evolution of hydrogen chloride began. If desired, the reaction could be hastened by the addition of 0.2 part of zinc chloride. After the evolution of gas subsided, the mass was heated to 200-210°C. and held there for an hour during which it was stirred. It was then cooled to 100°C. and 15 parts of glycerol and 50 parts of xylene added. After heating at 240-250°C. for 4 hours and removing the volatile substances under reduced pressure, a light-colored resin was obtained. It was soluble in hydrocarbon solvents, but not in aqueous alkalies. It had good elasticity and resistance to the weather. Other alcohols which may be substituted for glycerol are glycol and benzyl alcohol. In several cases the aralkyl halide employed was prepared by the action of 40 per cent formaldehyde and hydrochloric acid on xylene, diphenyl oxide or anisol.<sup>39</sup>

<sup>31</sup> F. Marschall, German P. 477,442, 1920, addn. to 416,904, 1920, to Farb. vorm. Meister, Lucius & Brüning; *Brit. Chem. Abs. B.*, 1926, 203.

<sup>32</sup> A. Voss, German P. 400,312, 1922, to Farb. vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1925, 44, 216.

<sup>33</sup> K. Schirmacher and A. Voss, German P. 446,999, 1921, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1928, 680.

<sup>34</sup> A. Voss, German P. 444,109, 1927, addn. to 416,109, 1925, to I. G. Farbenind. A.-G.; *Chem. Zentr.*, 1927, 2, 750.

<sup>35</sup> K. Daimler, F. Marschall and G. Balle, U. S. P. 1,635,883, July 12, 1927, to Grasselli Dyestuff Corp.; *Chem. Abs.*, 1927, 21, 2993. British P. 240,318, 1924, to Farbwerke vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1925, 44, 965B. K. Daimler and G. Balle, German P. 472,289, 1926, addn. to 426,881, 1924, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 2449.

<sup>36</sup> C. Winter and N. Roh, German P. 555,083, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 5221. British P. 361,951, 1930; *Brit. Chem. Abs. B.*, 1932, 357.

<sup>37</sup> G. Städtikov and I. Goldfarb, *Ber.*, 1928, 61, 2341; *Chem. Abs.*, 1929, 23, 1408.

<sup>38</sup> G. Kränzlein and A. Voss, U. S. P. 1,952,676, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3605. French P. 740,162, 1922; *Chem. Abs.*, 1933, 27, 2820. German P. 570,958, 1933; *Chem. Abs.*, 1933, 27, 4430. British P. 392,392, 1932; *Brit. Chem. Abs. B.*, 1933, 800. See also C. Winter and N. Roh, German P. 564,127, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1220.

<sup>39</sup> For the preparation of 1-(chloromethyl)naphthalene by this reaction see, G. Reddlien and H. Sange, U. S. P. 1,910,475, May 28, 1933, to General Aniline Works; *Chem. Abs.*, 1933, 27, 3953.

Makarov and Andrianov<sup>40</sup> report that casein and benzyl chloride react in the presence of alkalis to form resins. Kirchhof<sup>41</sup> has studied the action of benzyl chloride on rubber using aluminum chloride as a catalyst. White to yellow, easily pulverized, thermoplastic products were formed. They were inert to alkalies and acids (other than nitric acid) and had good insulating properties.

**Aralkyl Halides and Phenols.** Condensation between benzyl chloride and phenolic compounds forms resins whose properties are dependent upon the phenolic body used. In general the resins formed from phenols and aralkyl chlorides are soluble in alcohols, whereas those from aromatic hydrocarbons and aralkyl chlorides are insoluble in alcohol. One mol each of phenol and benzyl chloride are heated without a catalyst on an oil bath (reaction begins at 130°C. and is completed by slowly raising the temperature to the boiling point of benzyl chloride), until the evolution of hydrochloric acid ceases, yields a clear, bright brown, thinly fluid oil which is soluble in dilute caustic soda solution.<sup>42</sup> An excess of phenol and zinc (as a catalyst) furnishes p-hydroxydiphenylmethane.<sup>43</sup> On the other hand, when equal parts of benzyl chloride and phenol were heated in the presence of franconite a plastic mass resulted.<sup>44</sup>

Chloromethylnaphthalene condenses with phenol to form a hard resin which is soluble in drying oils.<sup>45</sup> Benzyl chloride and  $\alpha$ -naphthol yield a thick, brown oil.<sup>46</sup>

Phenolic acids and their derivatives may also be reacted with benzyl and other aralkyl halides.<sup>47</sup> Many catalysts may be used including zinc, aluminum, iron, their halides and fuller's earth. The resinous materials are soluble in linseed oil, tung oil and turpentine and so may be employed in making varnish.<sup>48</sup> Among the combinations that have been suggested are dimethyl benzyl chloride with salicylic acid, dimethyl benzyl chloride with phenyl salicylate, dimethyl benzyl chloride with acetyl salicylic acid, isopropyl benzyl chloride with salicylic acid and 1,2,3,4-tetrahydro-6- $\omega$ -chloromethylnaphthalene with 2-hydroxy-3-methylbenzoic acid.

Resins from aralkyl halides and phenols are rendered soluble in water by sulphonation.<sup>49</sup> Doser and Thauss<sup>50</sup> made water-soluble substances by sulphonating the reaction products of aralkyl halides with rosin and phenols. For example, a resin was prepared by mixing 30 parts of rosin and 10 parts of phenol in the presence of 1.5 parts of 60° Be. sulphuric acid and heating to 70-80°C. for 8 hours. Then, 10 parts of this resin was treated at 110-120°C. with 3 parts of benzyl chloride and 0.2 part of zinc chloride. The final product was sulphonated with 2 parts of 100 per cent sulphuric acid. The original phenol-rosin resin can

<sup>40</sup> B. V. Makarov and K. A. Andrianov, Russian P. 30,276, 1933; *Chem. Abs.*, 1933, 27, 5562.

<sup>41</sup> F. Kirchhof, *Kautschuk*, 1931, 7, 128; *Chem. Abs.*, 1931, 25, 6015. *Rubber Chem. Tech.*, 1932, 5, 110; *Chem. Abs.*, 1933, 27, 6016. German P. 557,270, 1930; *Chem. Abs.*, 1933, 27, 446.

<sup>42</sup> German P. 346,384, 1917, to Kalle & Co. A.-G.; *J.S.C.I.*, 1922, 41, 510A.

<sup>43</sup> T. Zincke and W. Walter, *Ann.*, 1904, 334, 373; *J.C.S.*, 1904, 86 (1), 1005.

<sup>44</sup> E. Freund and H. Jordan, German P. 417,668, 1921, to Chem. Fabr. auf Actien vorm. E. Schering; *Brit. Chem. Abs. B*, 1926, 100.

<sup>45</sup> G. Kränlein, A. Voss and A. Brunner, German P. 526,391, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 4423. German P. 561,082, 1930, addn. to 526,391, 1929; *Chem. Abs.*, 1933, 27, 1220. German P. 551,169, 1929; *Chem. Abs.*, 1932, 26, 4488. French P. 695,476, 1930; *Chem. Abs.*, 1931, 25, 2867. British P. 360,888, 1930; *Chem. Abs.*, 1933, 27, 1230.

<sup>46</sup> German P. 346,384, 1917, to Kalle & Co. A.-G.; *J.S.C.I.*, 1922, 41, 510A.

<sup>47</sup> German P. 346,384, 1917, to Kalle & Co. A.-G.; *J.S.C.I.*, 1922, 41, 510A.

<sup>48</sup> C. Winter and N. Roh, U. S. P. 1,977,979, Oct. 28, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 253. British P. 382,301, 1933; *Chem. Abs.*, 1933, 27, 4431.

<sup>49</sup> British P. 332,960, 1929, addn. to 320,056, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 1017. French P. 83,268, 1930, addn. to 663,155, 1928; *Chem. Abs.*, 1932, 26, 1077.

<sup>50</sup> A. Doser and A. Thauss, U. S. P. 1,762,011, June 3, 1930, to General Aniline Works, Inc.; *Chem. Abs.*, 1930, 24, 3658. See also A. Doser, G. Mauthe and A. Thauss, U. S. P. 1,823,033, Oct. 20, 1931, to General Aniline Works, Inc.; *Chem. Abs.*, 1932, 26, 362.

be sulphonated before condensation with benzyl chloride. Likewise, phenol sulphonic acids may be condensed with aralkyl halides.<sup>61</sup>

**Benzal-Halide Resins.** Benzal chloride is very sensitive to resinification. Dissolved in carbon disulphide and treated with aluminum chloride, it forms a hard, insoluble product even at low temperatures.<sup>62</sup> Iron carbonate reacts vigorously with benzal chloride at 60°C. with formation of a black resinous mass,<sup>63</sup> and zinc oxide at 100°C. produces large quantities of tar unless a solvent is present.<sup>64</sup> On addition of zinc dust, a mixture of benzal chloride and aniline forms 4,4'-diaminotriphenylmethane and much resin.<sup>65</sup>

Condensation of benzal chloride or xylene dichloride with naphthalene, phenanthrene or anthracene yields resins which are hard in comparison with the oily products obtained from a mixture of benzyl chloride and polynuclear hydrocarbons. Iron may be used as a condensing agent.<sup>66</sup> The resins are readily soluble in hydrocarbon solvents and have been recommended as impregnating and coating agents,<sup>67</sup> or mixed with cellulose ethers to form plastic masses.<sup>68</sup> To make the resins still harder, they may be treated with formaldehyde<sup>69</sup> or blown with air<sup>70</sup> as was the case with the oily products from benzyl and xylyl chlorides.

Resins are obtained when benzal chloride is heated with either phenol, in the presence of zinc chloride at 50-100°C., or with m-cresol, in the presence of aluminum chloride at 70°C., until hydrogen chloride is no longer evolved, and the excess phenol or cresol is removed by steam distillation. An odorless, light-colored resin, which is soluble in caustic alkalis, alcohols and chloroform is produced. Similar products result from homologues of benzal chloride or from derivatives containing halogen in the nucleus.<sup>61</sup> Mackenzie<sup>62</sup> used 55 g. of phenol with 16.9 g. of benzal chloride without a catalyst. Heating the mixture gently at first and then gradually raising the temperature to 120°C. for 10 hours, he obtained a dark brown residue which on vacuum distillation (to remove excess phenol) changed to a ruby-red, transparent jelly. This jelly crystallized readily yielding dihydroxy-triphenylmethane.

Benzal bromide (25 parts) and Swedish rosin (140 parts) were fused together by Kränzlein and Voss.<sup>63</sup> As the reaction proceeded the mixture became so thick that it could no longer be stirred. To avoid this, chlorobenzene was added and the mass held at 200-210°C. for 2 hours. The volatile constituents were removed at 200°C. by reducing the pressure and the product esterified by refluxing with glycol for 5-6 hours. After distilling the volatile constituents, a resin was obtained which was soluble in drying oils producing varnishes with good resistance to light.

<sup>61</sup> British P. 320,056, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1930, 315. French P. 663,155, 1928; *Chem. Abs.*, 1930, 24, 735.

<sup>62</sup> J. Boeseken, *Rec. trav. chim.*, 1903, 22, 312; *Chem. Zentr.*, 1903, 2, 202.

<sup>63</sup> J. J. Vanin and A. A. Tschernojarova, *J. Russ. Phys.-Chem. Soc.*, 1927, 59, 891; *Brit. Chem. Abs.* A, 1928, 758.

<sup>64</sup> W. Davies and J. H. Dick, *J.C.S.*, 1932, 2808.

<sup>65</sup> C. Böttinger, *Ber.*, 1879, 12, 975; *Chem. Zentr.*, 1879, 456.

<sup>66</sup> German P. 302,521, 1916, addn. to 301,713, 1916, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1921, 40, 708A.

<sup>67</sup> German P. 302,531, 1917, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1921, 40, 344A.

<sup>68</sup> German P. 336,476, 1918, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1921, 40, 577A.

<sup>69</sup> K. Schirmacher and A. Voss, German P. 446,999, 1921, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1923, 680.

<sup>70</sup> A. Voss, German P. 400,312, 1922, to Farbwerke vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1925, 44, 216B.

<sup>61</sup> German P. 355,389, 1920, to Dynamit-A.-G. vorm. A. Nobel & Co.; *J.S.C.I.*, 1922, 41, 772A.

<sup>62</sup> J. E. Mackenzie, *J.C.S.*, 1901, 79, 1216.

<sup>63</sup> G. Kränzlein and A. Voss, U. S. P. 1,952,676, Mar. 27, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3605. French P. 740,163, 1922; *Chem. Abs.*, 1923, 27, 2320. German P. 570,958, 1933; *Chem. Abs.*, 1933, 27, 4430. British P. 392,353, 1932; *Brit. Chem. Abs.* B, 1933, 800.

**Benzotrichloride Resins.** Döbner<sup>64</sup> described various condensation reactions of benzotrichloride and noted the tendency to resin formation in many of these. From benzotrichloride and phenol, he obtained both dihydroxytriphenylcarbinol and a yellow resin. Döbner and Schröter<sup>65</sup> added 46 g. of benzotrichloride drop by drop to 50 g. of o-cresol on a water bath. The product, freed from excess cresol by treatment with steam, consisted of a dye and a resin. Treatment with hot sodium bisulphite solution dissolved the dye leaving a yellow resin. Reactions between  $\alpha$ - and  $\beta$ -naphthol<sup>66</sup> and pyrogallol<sup>67</sup> with benzotrichloride are reported as producing resinous substances along with crystallizable bodies.

Heiber<sup>68</sup> treated a solution of sodium phenolate (containing 3 mols of phenol) with 1 mol of benzotrichloride, heating on a water bath until the odor of the chloride had disappeared. After acidifying and washing with water to remove excess phenol, the product yielded on distillation with steam a bright-yellow distillate and a reddish-yellow, resinous residue. The distilled oil was shown by Heiber to contain phenyl benzoate and what was believed to be o-hydroxybenzophenone. The same products were obtained by Hamada.<sup>69</sup>

Ellis<sup>70</sup> prepared a resin by heating 3 mols of phenol with 1 mol of crude benzotrichloride (chlorinated toluene) in alcoholic solution (at its boiling point) in the presence of ferric or aluminum chloride. The mass became insoluble and infusible within an hour, if aluminum chloride was used as the catalyst. If no condensing agent was added, the reaction occurred in two stages, first with the formation of a syrupy liquid (within 40 minutes) which on further heating lost water and became dark brown and semi-solid. Ultimately a solid resin resulted. When the syrupy product was heated with formaldehyde solution (40 per cent), it was converted into a tough, red, rubbery mass which hardened on further heating.<sup>71</sup> The addition of 10 per cent hexamethylenetetramine greatly accelerated hardening.<sup>72</sup> Prior to treatment with formaldehyde, excess phenol may be removed by steam distillation.<sup>73</sup>

A hard resin is produced by the condensation of benzotrichloride with aniline. This reaction occurs in two stages, yielding first a dark green, heavy oil and finally a dark red resin. Paraformaldehyde or hexamethylenetetramine accelerates hardening of the resin. Condensation of benzotrichloride with benzene (2 mols) in the presence of anhydrous aluminum chloride yields a resin easily soluble in benzene, together with a small amount of triphenylcarbinol and benzoic ester.<sup>74</sup>

Wohl and Wertyporoch<sup>75</sup> studied the action of aluminum chloride on benzotrichloride. Five per cent of aluminum chloride was added and after the mixture had been heated for 4 hours at 50-60°C., it yielded m-trichloromethyl-diphenyldichloromethane, m-(m-trichloromethyl-dichlorobenzyl)diphenyldichloromethane and a highly polymerized, insoluble resin containing chlorine. Either of the diphenyldichloromethane derivatives could be converted into higher condensates and resins by heating further with aluminum chloride. Such compounds are therefore to be regarded as resin intermediates. This would indicate that the course of

<sup>64</sup> O. Döbner, *Ann.*, 1883, 217, 223; *J.C.S.*, 1883, 44, 861. R. Meyer and W. Gerloff (*Ber.*, 1923, 56, 98; 1924, 57, 591; *Chem. Abs.*, 1923, 17, 1221; 1924, 18, 2889) have studied reactions similar to these but have not reported the formation of resins.

<sup>65</sup> O. Döbner and G. Schröter, *Ann.*, 1890, 257, 68; *J.C.S.*, 1890, 58, 898.

<sup>66</sup> O. Döbner, *Ann.*, 1890, 257, 56; *J.C.S.*, 1890, 58, 901.

<sup>67</sup> O. Döbner and A. Förster, *Ann.*, 1890, 257, 60; *J.C.S.*, 1890, 58, 899.

<sup>68</sup> F. Heiber, *Ber.*, 1891, 24, 3684; *J.C.S.*, 1892, 62, 308. Cf. O. Döbner and W. Stackmann, *Ber.*, 1876, 9, 1918; *J.C.S.*, 1877, 32 (2), 327.

<sup>69</sup> C. Hamada, *Science Repts. Tohoku Imp. Univ.*, 1932, 22, 55; *Chem. Abs.*, 1933, 27, 3928.

<sup>70</sup> Carleton Ellis, U. S. P. 1,793,810, Feb. 17, 1931, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 2312.

<sup>71</sup> Carleton Ellis, U. S. P. 1,793,811, Feb. 17, 1931, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 2312.

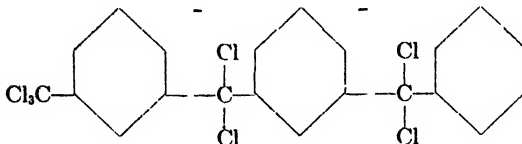
<sup>72</sup> Carleton Ellis, U. S. P. 1,793,812, Feb. 17, 1931, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 2312.

<sup>73</sup> B. N. Lougovoy, U. S. P. 1,648,852, Nov. 8, 1927, to Ellis-Foster Co.; *Chem. Abs.*, 1928, 22, 504.

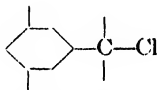
<sup>74</sup> Experimental work carried out in the author's laboratory.

<sup>75</sup> A. Wohl and E. Wertyporoch, *Ann.*, 1930, 481, 30; *Chem. Abs.*, 1930, 24, 4397.

resinification of benzotrichloride in the presence of aluminum chloride involves initial formation of chains which may be represented:



Probably only one<sup>76</sup> of the chlorine-atoms of each  $\text{CCl}_2$ -group is involved in this condensation; and, since combination may occur at any free meta position, the final insoluble polymer would correspond to a structure consisting of groupings that may be represented:



Tars are formed by the action of cadmium and lead oxides on benzotrichloride.<sup>77</sup>

**Resins from Naphthalene Chlorides.** The chlorine addition products of naphthalene<sup>78</sup> behave in a manner analogous to the other aralkyl chlorides. When heated with aluminum chloride, naphthalene tetrachloride is resinified and the resin so obtained is soluble in benzene, turpentine and linseed oil, but insoluble in alcohol. Its use in the manufacture of varnishes and lacquers has been recommended. Another procedure consists in dissolving 100 parts of naphthalene tetrachloride in 400 parts of toluene, adding 3.5 parts of aluminum chloride and heating for several hours on a water bath. The solvent is expelled by distilling with steam and the resin freed from moisture by further heating to  $150^\circ\text{C}$ . A clear, brittle resin is obtained. A similar product is formed by heating a mixture of 300 parts of xylene, 100 parts of naphthalene tetrachloride and 3 parts of ferric chloride, first on a water bath and then for several hours at  $130^\circ\text{C}$ . The crude chlorinated material, a mixture of naphthalene di- and tetrachlorides prepared by chlorinating 256 parts of naphthalene in 800 parts of chloroform until about 3.5 atoms of chlorine have been added, may be converted to resin by several hours heating with 20 parts of aluminum chloride. Antimony pentachloride also acts as a condensing agent. A hard resin is made from the dichloro derivative of tetrahydronaphthalene by adding 5 per cent of aluminum chloride and heating to  $200^\circ\text{C}$ . By dissolving 30 parts of the dichloro derivative in 120 parts of toluene, adding 1 part of aluminum chloride and boiling the mixture under reflux for several hours a semi-solid resin is obtained whose solution in benzene dries to a varnish-like coating. More highly chlorinated derivatives of tetrahydronaphthalene yield brittle resins when heated to  $250^\circ\text{C}$ . in the presence of 0.7 per cent of ferric chloride. The bromine derivatives yield similar resins.<sup>79</sup>

Naphthalene chlorides heated (without solvents) with a small amount of a metal or metallic compound yield hard resins, e.g., naphthalene tetrachloride heated to  $215^\circ\text{C}$ . with 0.5 per cent of ferric oxide.<sup>80</sup> This resin when dissolved in acetone

<sup>76</sup> O. Döbner (*Ann.*, 1833, 217, 226; *J.C.S.*, 1833, 44, 361) noted that one of the chlorine atoms of benzotrichloride cannot be displaced by aromatic groups.

<sup>77</sup> W. Davies and J. H. Dick, *J.C.S.*, 1932, 2808.

<sup>78</sup> Naphthalene chlorides such as naphthalene tetrachloride,  $\text{C}_{10}\text{H}_6\text{Cl}_4$ , should not be confused with the chlorine substitution products of naphthalene such as tetrachloronaphthalene,  $\text{C}_{10}\text{H}_4\text{Cl}_4$ . The latter are analogous to chlorobenzene and are less prone to form resins by the above processes. Naphthalene chlorides are formed either by the chlorination of naphthalene in the dark and in the presence of a halogen-carrier or by the chlorination of tetrahydronaphthalene.

<sup>79</sup> German P. 332,391, 1918, to A.-G. für Anilin-Fabrik; *J.S.C.I.*, 1921, 40, 353A.

<sup>80</sup> E. Freund and H. Jordan, *German P.* 466,282, 1928, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1929, 23, 1000.



or carbon tetrachloride may be used as a lacquer.<sup>61</sup> Florenz added chlorine to anthracene and phenanthrene suspended in carbon disulphide or benzene and, after evaporating the solvent, treated the residues with condensing agents to form resins.<sup>62</sup> Anthracene dibromide with sodium acetate gives resinous products.<sup>63</sup>

Hydrosilicates of aluminum and magnesium, such as fuller's earth, franconite or tonsil, are capable of functioning as catalysts in the Friedel-Crafts reaction. When a mixture of equimolecular quantities of naphthalene and naphthalene tetrachloride is slowly heated with 0.1 per cent of fuller's earth to about 60°C., a vigorous evolution of hydrogen chloride takes place. After heating at 120°C. for 2 hours, the portion soluble in carbon tetrachloride is a dark green, brittle resin which softens at 65°C. Substitution of phenols (from low-temperature coal tar) for naphthalene gives a green mass which softens at 85°C. and is soluble in alcohol.<sup>64</sup> 1,2-Dibromo-ac-tetrahydronaphthalene, chlorinated decahydronaphthalene and pinene hydrochloride also give resins when heated with fuller's earth; and, under the same conditions, a solution of benzyl chloride in xylene forms a saturated viscous oil.<sup>65</sup>

In the presence of condensation agents, naphthalene chlorides react with formaldehyde to form hard resins.<sup>66</sup>

Resins soluble in benzene, chloroform, linseed oil, turpentine and alcohol are made by heating phenols with naphthalene chlorides in the presence of metal halides, with or without the addition of solvents. Typical examples are: Phenol heated to 90-95°C. with a solution of naphthalene tetrachloride in tetrachloroethane, and ferric chloride; o-cresol heated to 100°C. with a solution of naphthalene tetrachloride in o-dichlorobenzene; and ferric or aluminum chloride; and phenol heated to 100°C. with ferric chloride and the product obtained by chlorinating tetrahydronaphthalene at ordinary temperature until four atoms of chlorine have been added.<sup>67</sup>

**Alkyl and Acyl Halides.** In addition to reactions involving many types of alkyl halides, resins have been formed by the interaction of various alkyl and acyl halides on aromatic compounds. Shinkle<sup>68</sup> condensed aromatic hydrocarbons with ethylene dichloride in the presence of aluminum chloride. The products are reported as being resistant to abrasion, solvents and heat. They may be chlorinated to reduce the flexibility. Resins (from ethylene dichloride and benzene) mixed with rubber and sulphur and vulcanized give a material recommended for the manufacture of hoses which must be resistant to gasoline.<sup>69</sup> Or the resins, after alkylation which renders them soluble in petroleum hydrocarbons, may be used as thickening agents for hydrocarbon oils.<sup>70</sup>

A dark green, viscous oil is formed by boiling 40 parts of acetylene tetrabromide with 20 parts of xylene and 1 part of fuller's earth until evolution of

<sup>61</sup> E. Freund and H. Jordan, German P. 474,683, 1922, to Schering-Kahlbaum A.-G.; *Chem. Abs.*, 1929, 23, 3113.

<sup>62</sup> M. Florenz, German P. 420,443, 1922, to Bakelite G.m.b.H.; *Brit. Chem. Abs.* B, 1926, 502.

<sup>63</sup> E. de B. Barnett, J. W. Cook and M. A. Matthews, *Rec. trav. chim.*, 1925, 44, 217; *Chem. Abs.*, 1925, 19, 2488.

<sup>64</sup> E. Freund and H. Jordan, U. S. P. 1,570,460, Jan. 19, 1926, to Chem. Fabr. auf Aktien vorm. E. Schering; *Chem. Abs.*, 1926, 20, 832. British P. 202,997, 1923; *J.S.C.I.*, 1925 44, 46B. E. Freund, German P. 461,358, 1922, to Schering-Kahlbaum A.-G.; *Chem. Zentr.*, 1929, 1, 1052.

<sup>65</sup> E. Freund, U. S. P. 1,672,378, June 5, 1928, to Chem. Fabrik auf Aktien vorm. E. Schering; *Brit. Chem. Abs.* B, 1928, 532. E. Freund and H. Jordan, German P. 417,667, 1921, to Chem. Fabrik auf Aktien vorm. E. Schering; *Brit. Chem. Abs.* B, 1926, 100.

<sup>66</sup> E. Freund and H. Jordan, German P. 417,668, 1921; *Brit. Chem. Abs.* B, 1926, 100.

<sup>67</sup> German P. 324,710, 1918, to A.-G. für Anilin-Fabr.; *J.S.C.I.*, 1921, 40, 479A.

<sup>68</sup> S. D. Shinkle, British P. 407,948, 1932, to Naugatuck Chem. Co.; *Brit. Chem. Abs.* B, 1934, 512. British P. 415,953, 1934, addn. to 407,948; *Chem. Abs.*, 1935, 29, 854. French P. 743,753, 1933; *Chem. Abs.*, 1933, 27, 3789. See also German P. 326,729, 1918, to Badische Anilin- and Soda-Fabrik; *J.S.C.I.*, 1921, 40, 142A.

<sup>69</sup> S. D. Shinkle, British P. 415,954, 1934, to Naugatuck Chemical Co.; *Brit. Chem. Abs.* B, 1934, 974. French P. 43,916, 1934, addn. to 743,753, 1933; *Chem. Abs.*, 1935, 29, 1535.

<sup>70</sup> French P. 771,214 and 771,215, 1934, to Standard Oil Development Co.; *Chem. Abs.*, 1935, 29, 854.

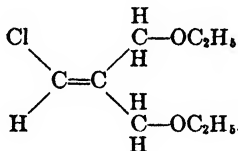
hydrogen bromide ceases.<sup>91</sup> Reaction between phenol and acetylene tetrabromide in aqueous alkali has been studied in the author's laboratory. Several products were obtained, one of which was a fusible resin. It could be hardened by boiling with formaldehyde in the presence of alkali and then adding hexamethylenetetramine.

The resinous by-products from the preparation of salicylaldehyde were also studied.<sup>92</sup> The yield of resin could be raised to 62 per cent by heating the mixture after the addition of the chloroform to the sodium phenolate solution for 3 hours instead of 30 minutes. This resin also could be hardened by the addition of 2 per cent of hexamethylenetetramine. Phenol and trichloroethylene likewise gave an oily substance which was hardened by boiling with formaldehyde solution and adding hexamethylenetetramine and could be used as a molding composition.

Mixtures of ethylene and propylene chlorohydrin were condensed with aniline and phenol. In the latter case both aluminum chloride and sulphuric acid were used as condensing agents. In the case of the aniline, boiling of the reactants in the presence of water was sufficient. The product, after treatment with paraldehyde and then hexamethylenetetramine, could be molded. It was a brittle, lustrous resin.

Reaction of aniline with carbon tetrachloride in the presence of a copper catalyst yielded a resin.<sup>93</sup> Similarly sodium anilide and trichloroethylene gave a red-black, tarry substance which was believed to consist of condensation products of aniline and monochloroacetylene.<sup>94</sup> Dichloroethylene also furnished a plastic mass when it was treated with formaldehyde under the catalytic influence of sulphuric acid.<sup>95</sup>  $\beta$ -Chloroethylaniline is said to be an unstable compound which polymerizes to a chlorine-free solid of unknown constitution.<sup>96</sup>

Kleinfeller and Frercks<sup>97</sup> attempted to bring about cyclizations leading to substances having an arrangement of carbon atoms similar to the diamond space lattice. They interacted 2-chloromethyl-1,3-dichloro-2-nitropropane and phloroglucinol in methyl alcohol in the presence of sodium methoxide. The products obtained were a reddish-brown resin and 1,3-diethoxy-3-chloromethylenepropane,



As the result of the reaction of cinnamyl chloride in nitrobenzene with phloroglucinol and aluminum chloride, Rosenmund and Rosenmund<sup>98</sup> obtained much resinous matter, a compound,  $\text{C}_{16}\text{H}_{12}\text{O}_4$ , and a substance melting at  $210^\circ\text{C}$ . Hexahydrodiphenylene oxide readily becomes resinified under the conditions of the Friedel-Crafts reaction, but with careful control it can be combined with acetyl chloride to give the corresponding methyl ketone.<sup>99</sup> Wieland and Hasegawa<sup>100</sup> described the reactions of acetyl and benzoyl chlorides with 1,4-diphenyl-1,3-butadiene in benzene in the presence of aluminum chloride. The crystallized prod-

<sup>91</sup> E. Freund and H. Jordan, U. S. P. 1,570,469, Jan. 10, 1926, to Chem. Fabrik auf Aktien vorm. E. Schering; *Chem. Abs.*, 1926, 20, 832. German P. 461,358, 1922; *Chem. Zentr.*, 1929, 1, 1052. British P. 202,997, 1923; *J.S.C.I.*, 1925, 44, 46B.

<sup>92</sup> Similar bodies are formed in the preparation of protocatechuic aldehyde. F. Tiemann and P. Koppe, *Ber.*, 1881, 14, 2015.

<sup>93</sup> R. C. Shah, *J. Indian Inst. Sci.*, 1934, 7, 205; *Chem. Abs.*, 1925, 19, 645.

<sup>94</sup> E. Vitoria, *Mem. acad. cienc. artes Barcelona*, 1928, 21, 227; *Chem. Abs.*, 1932, 26, 4799.

<sup>95</sup> H. J. Prins, *Rec. trav. chim.*, 1933, 51, 469; *Chem. Abs.*, 1933, 26, 3777.

<sup>96</sup> G. R. Clemo and W. H. Perkin, Jr., *J.C.S.*, 1924, 125, 1804.

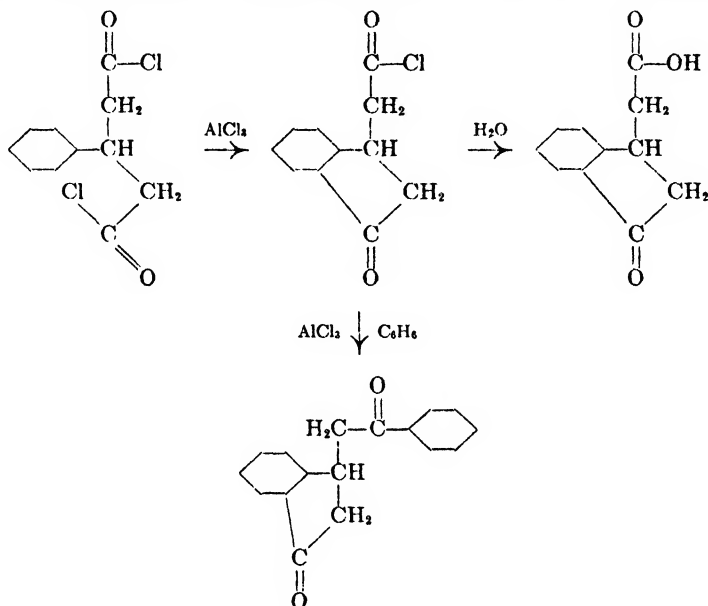
<sup>97</sup> H. Kleinfeller and W. Frercks, *J. prakt. Chem.*, 1933, (2) 136, 184; *Brit. Chem. Abs. A*, 1933, 1295.

<sup>98</sup> K. W. Rosenmund and M. Rosenmund, *Ber.*, 1928, 61, 2608; *Brit. Chem. Abs. A*, 1929, 825.

<sup>99</sup> J. von Braun, *Ber.*, 1922, 55, 3761; *J.C.S.*, 1923, 124 (1), 108.

<sup>100</sup> H. Wieland and C. Hasegawa, *Ber.*, 1931, 64, 2516. See also P. Lipp, P. Küppers and M. Hall, *Ber.*, 1927, 60, 1875.

ucts possessed quite high molecular weights pointing to complex condensations and polymerizations. The acetylchloride derivative possessed the formula,  $C_{20}H_{28}O_2Cl$ ; the benzoyl,  $C_{20}H_{20}O$ . Acetyl chloride and camphene in ether with aluminum chloride as a catalyst gave a large amount of resin. Jackson and Kenner added aluminum chloride to  $\beta$ -phenylglutaryl chloride in purified light petroleum and obtained a tar and 1-ketohydrindene-3-acetic acid. When benzene was present in the solution  $\omega$ -3-hydrindonylaceto-phenone was also formed. This is similar to the action of hydrocarbons in stopping the condensation of benzyl chloride.<sup>101</sup>



Pyridine will dissolve copper halides and so has been described as a catalyst in the condensations of organic halogen compounds in the presence of copper. Reactions involving the use of this combination are often accompanied by resin formation.<sup>102</sup>

Shellac substitutes have been produced by the condensation of fatty acids with "resinol"<sup>103</sup> or hydroaromatic acids. Combination can be accomplished in several ways. Chlorinated derivatives of the unsaturated fatty acids may be heated with the resinolic acid, or the chlorine derivatives of either fatty acids or resinolic acids may be condensed with the hydroxy derivatives of the other.<sup>104</sup> For example, trihydroxystearic acid was heated in the presence of aluminum chloride with chlorinated abietic acid. The latter was formed by passing chlorine into an alkaline solution of rosin and then precipitating with a mineral acid. Or the acids of linseed oil were chlorinated in benzene and heated with a solution of hydroxycyclohexanecarboxylic acid in benzene. Another modification was to chlorinate both reactants.<sup>105</sup>

<sup>101</sup> J. G. Jackson and J. Kenner, *J.C.S.*, 1928, 573.

<sup>102</sup> P. Karrer, W. Wehrli, E. Biedermann and M. D. Vedova, *Helv. Chim. Acta*, 1928, 11, 233; *Chem. Abs.*, 1928, 22, 1891.

<sup>103</sup> The resinol acids are the free acids contained in natural resins. They are, in general, complex bodies of high molecular weight and usually contain one or more hydroxyl groups. A. H. Allen, "Commercial Organic Analysis," P. Blakiston's Son & Co., Philadelphia, 3rd. Ed., 1907, II (3), 147. R. S. Morrell, "Varnishes and Their Components," H. Frowde and Hodder & Stoughton, London, 1923, 107.

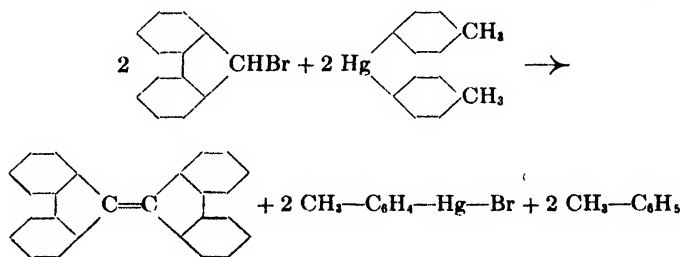
<sup>104</sup> J. Scheiber, U. S. P. 1,903,598, April 11, 1933, to W. Dux; *Chem. Abs.*, 1933, 27, 3350. British P. 309,956, 1928; *Brit. Chem. Abs. B*, 1930, 26. German P. 504,328, 1927; *Chem. Abs.*, 1931, 25, 610.

<sup>105</sup> J. Scheiber, U. S. P. 1,927,472, Sept. 19, 1933; *Chem. Abs.*, 1933, 27, 5993.

Prins<sup>106</sup> investigated the reactions of chlorinated paraffins with chloro-olefins. Chloroform condensed with tetrachloroethylene in the presence of aluminum chloride to give heptachloropropane. The reaction went most rapidly with monochloroethylene. Sometimes higher condensation products were isolated due to the loss of hydrogen chloride and formation of reactive chloropropenes or, more generally, of an unsaturated compound with a vicinal trichloromethyl or dichloromethylene group.

Resinous compounds which can be added to lubricating oils to improve their viscosity, color and pour points, are made by combining chlorinated wax (containing 20 per cent chlorine) with naphthalene, using aluminum chloride as a catalyst.<sup>107</sup> Only a small proportion, 0.2-1.0 per cent, of the resin need be incorporated with the oil. An alternative procedure consists in fractionally precipitating (by cooling) the chlorinated wax from a solvent, and treating the individual fractions with naphthalene.<sup>108</sup> Or the separate fractions may be polymerized by the action of aluminum chloride and the polymers used as described above.

**Miscellaneous Condensations.** Angeletti in attempting to prepare the 2-halo-2'-nitro-6,6'-bitolyls by the Sandmeyer reaction on dl-2-amino-2'-nitro-6,6'-bitolyl obtained tars and resins as by-products.<sup>109</sup> Koller<sup>110</sup> tried to obtain 1,8-naphthyridine by reducing 2,4-dichloronaphthyridine. With hydrogen and palladium a mixture of chlorinated and hydrogenated derivatives of naphthyridine resulted. This could not be distilled since it resinified on heating. Resinification interfered with the preparation of cyanoanthrones from chloroanthrones.<sup>111</sup> In the presence of condensing agents chlorinated naphthalenes which contain one hydrogen atom may be combined with glycolic acid, glycolide or oxalic acid.<sup>112</sup> Tribromophenol bromide loses bromine very readily to form amorphous products.<sup>113</sup> Oxidation of trichlorophenol produced polynuclear quinones and also an amorphous oxide.<sup>114</sup> Refluxing a toluene solution of 9-bromofluorene and mercury di-p-tolyl gave a tarry mass from which bis-diphenylene ethylene was isolated.<sup>115</sup>



<sup>106</sup> H. J. Prins, *Rec. trav. chim.*, 1932, 51, 1065; *Chem. Abs.*, 1933, 27, 489.

<sup>107</sup> British P. 415,065, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 921. See also F. H. MacLaren, U. S. P. 1,963,917 and 1,963,918, June 19, 1934, to Standard Oil Co. of Ind.; *Chem. Abs.*, 1934, 28, 5226. G. H. B. Davis, U. S. P. 1,815,022, July 14, 1931, to Standard Oil Development Co.; *Chem. Abs.*, 1931, 25, 5283. For a discussion of pour-point depressors, or "Parafflow," see G. H. B. Davis and A. J. Blackwood, *Ind. Eng. Chem.*, 1931, 23, 1452. G. H. B. Davis, *National Petroleum News*, 1932, 24 (52), 32, 34; *Chem. Abs.*, 1933, 27, 1494. Chlorination of various petroleum fractions is discussed in Chapter 10.

<sup>108</sup> British P. 417,659, 1933, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1935, 13.

<sup>109</sup> A. Angeletti, *Gazz. chim. ital.*, 1931, 61, 832; *Chem. Abs.*, 1932, 26, 1919. See also L. Mascarelli, D. Gatti and M. Pirona, *Gazz. chim. ital.*, 1931, 61, 782; *Chem. Abs.*, 1932, 26, 1595.

<sup>110</sup> G. Koller, *Ber.*, 1927, 60, 1572; *Chem. Abs.*, 1927, 21, 3203.

<sup>111</sup> E. de B. Barnett and C. L. Hewett, *J.C.S.*, 1932, 506.

<sup>112</sup> H. Bosshard and D. Strauss, German P. 298,258, 1920, to Elektrochem. Werke G.m.b.H.; *J.S.C.I.*, 1924, 43, 879B. Cf. British P. 171,960, 1921, *J.S.C.I.*, 1922, 41, 676A.

<sup>113</sup> R. Benedikt, *Ann.*, 1879, 199, 127; *J.C.S.*, 1880, 38, 246. See also W. M. Lauer, *J.A.C.S.*, 1926, 48, 442.

<sup>114</sup> W. H. Hunter and M. Morse, *J.A.C.S.*, 1928, 48, 1615.

<sup>115</sup> F. C. Whitmore and E. N. Thurman, *J.A.C.S.*, 1929, 51, 1491.

The residue obtained by distilling together ethyl 1,4-dibromobutane-1,1,4,4-tetracarboxylate and phenol yielded, on boiling with hydrochloric acid, adipic acid and a dark gum.<sup>116</sup>

Schaarschmidt and Raack<sup>117</sup> attempted to prepare nitrosobenzene by the action of nitrosyl chloride on benzene in the presence of aluminum chloride. The principal purified compound from 65 g. of nitrosyl chloride, 240 g. of benzene and 270 g. of aluminum chloride was 55 g. of p-aminobiphenyl which was accompanied by 120 g. of an indefinite, brown product. Benzene and aluminum bromide on long standing produce a resin.<sup>118</sup>

Shoesmith<sup>119</sup> has stated that the hydroxybenzyl alcohols resulting from the hydrolysis of  $\omega$ -chlorotolyl carbonates show a very strong tendency to resinify in the presence of acids. Diphenyl- $\alpha$ -naphthylchloromethane in benzene, when kept in contact with mercuric oxide for several days, gives a 50 per cent yield of diphenyl- $\alpha$ -naphthyl carbinol. The remainder is precipitated as a gum by petroleum ether.<sup>120</sup>

Bigot<sup>121</sup> found among the reaction products of 3-chloro-1,2-epoxypropane (dissolved in ether) and sodium, an insoluble rubber-like material. The preparation of di-p-chlorobenzoyl propane from glutaryl chloride and chlorobenzol is accompanied by resinification.<sup>122</sup>

The treatment of diphenylaminocyclobutane carboxylic acid in ether solution with nitrosyl bromide gives a lactone. A resin is left in solution in the mother liquor.<sup>123</sup>

**Resins by the Würtz-Fittig Reaction.** In the reaction of chlorobenzene with sodium only a small amount of resinous material is obtained,<sup>124</sup> but when more highly substituted compounds, such as p-dibromobenzene,<sup>125</sup> are used, the products are resinous. If the reaction of p-dibromobenzene and sodium is conducted in ether, a polymer with a composition corresponding to  $C_{16}H_{12}Br_2$  is formed after three days. Higher polymers are formed after a longer time.<sup>126</sup> Jacobson<sup>127</sup> considers the molecular structure of these polymers to be p-phenylene chains with bromine atoms at each end:



The polymers are soluble but infusible. In liquid ammonia a tar is obtained from o-dichlorobenzene and sodium.<sup>128</sup> p-Xylylene dibromide<sup>129</sup> reacts with sodium in toluene to give an insoluble, infusible polymer of the empirical formula,  $(C_8H_6)_n$ , isomeric with polystyrene.<sup>130</sup> The constitution of the material may be represented as a long chain of xylylene-groups,  $(-CH_2-C_6H_4-CH_2-)_n$ .

In the preparation of Grignard reagents from dihalogenated benzene, tars are produced.<sup>131</sup> With p-dibromobenzene some p-dibromobiphenyl was isolated. Acetyl bromide and magnesium in ether give diacetyl and a resin. The product of the

<sup>116</sup> J. J. Lennon and W. H. Perkin, Jr., *J.C.S.*, 1928, 1524.

<sup>117</sup> A. Schaarschmidt and M. Raack, *Ber.*, 1925, 58, 348; *Chem. Abs.*, 1925, 19, 1567.

<sup>118</sup> E. Wertyporoch and H. Sagel, *Ber.*, 1933, 66, 1306; *Chem. Abs.*, 1934, 28, 116.

<sup>119</sup> J. B. Shoesmith, *J.C.S.*, 1923, 123, 2698.

<sup>120</sup> J. O. Halford, *J.A.C.S.*, 1929, 51, 2158.

<sup>121</sup> A. Bigot, *Ann. chim. phys.*, 1891, 22, 433; *Chem. Zentr.*, 1891, 1, 963.

<sup>122</sup> S. Skraup and S. Guggenheimer, *Ber.*, 1925, 58, 2488.

<sup>123</sup> R. Stoermer and F. Schenck, *Ber.*, 1928, 61, 2317.

<sup>124</sup> W. E. Bachmann and H. T. Clarke, *J.A.C.S.*, 1927, 49, 2089. In hot dimethylaniline a nitrogen-containing pitch is formed.

<sup>125</sup> F. Riese, *Ann.*, 1872, 164, 161; *J.C.S.*, 1878, 26, 62.

<sup>126</sup> G. Goldschmidt, *Monatsh.*, 1886, 7, 42; *J.C.S.*, 1886, 50, 541.

<sup>127</sup> R. A. Jacobson, *J.A.C.S.*, 1932, 54, 1513.

<sup>128</sup> C. A. Kraus and G. F. White, *J.A.C.S.*, 1923, 45, 768.

<sup>129</sup> R. A. Jacobson, *J.A.C.S.*, 1932, 54, 1513.

<sup>130</sup> See Chapter 11.

<sup>131</sup> Y. Zalkind and P. V. Ragovina, *J. Russ. Phys.-Chem. Soc.*, 1927, 59, 1013; *Chem. Abs.*, 1928, 22, 5398. See also M. A. Mihailescu and St. P. Caragea, *Bull. sect. sci. acad. roumaine*, 1929, 12 (4/5), 7; *Chem. Abs.*, 1930, 24, 2116.

decomposition with water also contains ethyl acetate.<sup>132</sup> The substance from the reaction of magnesium with 1,4-dibromonaphthalene is converted by water into naphthalene, 1-bromonaphthalene and resinous matter.<sup>133</sup> 1,2-Dibromonaphthalene and magnesium also give tarry matter. Triphenylmagnesium bromide yields tars or oils when treated with oxygen, thionyl chloride and triphenylchloromethane.<sup>134</sup>

2,2'-Diiodobiphenyl and o-iodobromobenzene when heated with copper gave resinous products.<sup>135</sup>

## CLASS II. RESINS BY HALOGENATION

In this class of compounds which owe, as has been said before, their resinous properties to the fact that they are complex mixtures of individuals, the principal members are the chlorinated biaryls and naphthalenes. The first of these have come into use due to the commercial preparation of biphenyl. However their applications, principally as insulators for condensers and transformers, thus far are very limited. The older method of synthesizing biphenyl, which was discovered by Berthelot, consisted of passing benzene through a hot tube.<sup>136</sup> This process has since been modified in that benzene vapor, preheated to 650°C., is brought in contact with liquids such as molten lead or metal salts at about 800°C. A certain per cent of higher homologues is also formed and, if desired, this percentage may be increased by raising the temperature.<sup>137</sup>

Williams<sup>138</sup> made polyphenyls, which are oily or waxy materials, by heating (to 650-950°C.) a mixture of benzene and biphenyl with 0.1 per cent or more of sulphur, hydrogen sulphide, carbon disulphide or sulphur dioxide.

**Preparation of Halogenated Biaryls.** The early investigators chlorinated biphenyl in the presence of various catalysts. Kramers<sup>139</sup> used antimony chloride and an amount of chlorine equivalent to the monochloro derivative. The products that he isolated were 2- and 4-chlorobiphenyl, 4,4'-dichlorobiphenyl and a high-boiling residue. Schmidt and Schultz<sup>140</sup> used iodine as a catalyst and obtained 4,4'-dichlorobiphenyl. Weber and Sölscher<sup>141</sup> found that at high temperatures chlorination gave tarry products which interfered with the crystallization of the less highly chlorinated compounds. Merz and Weith<sup>142</sup> noted that a bright brown, resinous mass was formed when crude chlorobiphenyl was heated.

Later, Jenkins<sup>143</sup> observed that iron was a good catalyst for the chlorination of biphenyl and that by controlling temperature, time and rate of flow of chlorine it is possible to vary and greatly increase the degree of chlorination. In his process an iron vessel is employed, around which is wound a coil for regulation of the temperature. The vessel is filled with iron packing material and molten biphenyl poured in until the catalyst is just covered. Chlorine is forced up

<sup>132</sup> D. V. Tistchenko, *Bull. soc. chim.*, 1925, (4) 37, 623; *J.C.S.*, 1925, 128 (1), 775.

<sup>133</sup> Y. Zalkind, J. Sergeev, L. Levin and A. Ergorov, *Ber.*, 1934, 67, 1031.

<sup>134</sup> C. F. Koelsch, *J.A.C.S.*, 1932, 54, 2045.

<sup>135</sup> L. Mascarelli, D. Gatti and B. Longo, *Gazz. chim. ital.*, 1933, 63, 661; *Chem. Abs.*, 1934, 28, 1686.

<sup>136</sup> Berthelot, *Ann. chim. phys.*, 1866 (4), 9, 454.

<sup>137</sup> T. E. Warren and C. B. Durgin, U. S. P. 1,891,514, Dec. 20, 1932, to Swann Research, Inc.; *Chem. Abs.*, 1933, 27, 1896. T. J. Scott, U. S. P. 1,894,283, Jan. 17, 1933, to Swann Research, Inc.; *Brit. Chem. Abs. B*, 1933, 907. British P. 312,902, 1923, to Federal Phosphorus Co.; *Chem. Abs.*, 1930, 24, 806. C. B. Durgin and R. L. Jenkins, U. S. P. 1,894,266, Jan. 17, 1933, to Swann Research, Inc.; *Brit. Chem. Abs. B*, 1933, 907. F. X. Govers, French P. 693,230, 1929; *Chem. Abs.*, 1930, 24, 4524. See also J. N. Carothers, U. S. P. 1,875,317, Sept. 6, 1932, to Swann Research, Inc.; *Chem. Abs.*, 1933, 27, 103. E. Tschunker and W. Klein, U. S. P. 1,957,968, May 8, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 4038.

<sup>138</sup> W. H. Williams, U. S. P. 1,976,468, Oct. 9, 1934, to Dow Chem. Co.; *Chem. Abs.*, 1934, 28, 7263.

<sup>139</sup> J. G. Kramers, *Ann.*, 1877, 189, 142; *Chem. Zentr.*, 1877, 824.

<sup>140</sup> H. Schmidt and G. Schultz, *Ann.*, 1831, 207, 339; *J.C.S.*, 1881, 40, 909.

<sup>141</sup> A. Weber and C. Sölscher, *Ber.*, 1883, 16, 882.

<sup>142</sup> V. Merz and W. Weith, *Ber.*, 1883, 16, 2882; *J.C.S.*, 1884, 46, 588.

<sup>143</sup> E. L. Jenkins, U. S. P. 1,892,397, Dec. 27, 1932, to Swann Research, Inc.; *Chem. Abs.*, 1933, 27, 1897. British P. 368,708, 1929, to Federal Phosphorus Co.; *Chem. Abs.*, 1932, 26, 4835. French P. 703,316, 1930; *Chem. Abs.*, 1931, 25, 4283.

through the biphenyl and at the top of the container an outlet is provided for the escape of hydrogen chloride. Since chlorination proceeds with considerable evolution of heat, cooling water is circulated at the start through the coil to keep the temperature at about 80°C. If the monochloro product is desired, the temperature is gradually decreased to 66°C. and chlorination stopped when the weight of the reaction mixture has increased by an amount equal to 80-95 per cent of that required for complete monochlorination. The product, washed with water to remove chlorides of iron and distilled, yields 50-80 per cent monochlorobiphenyl. To make higher-chlorinated products, the temperature is allowed to rise to 175-220°C. during the progress of the reaction. At these temperatures, according to Jenkins, it is possible to chlorinate smoothly and rapidly to a mixture of chlorobiphenyls with an average chlorine content of 70 per cent. The degree of chlorination can be found by determining the specific gravity of samples of the product;

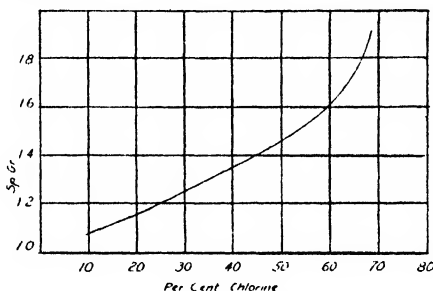


FIG. 148.—Specific Gravity as a Function of Chlorine Content in Chlorinated Biphenyl. (R. L. Jenkins.)

Figure 148 shows the relation between the specific gravity and chlorine content as determined by Jenkins.

Another process involves chlorination at a temperature slightly above the melting point. Antimony chloride is used as a catalyst.<sup>144</sup> In the presence of carriers, Britton and Stoesser<sup>145</sup> chlorinated biphenyl in various solvents at -10 to 40°C. Among the solvents used were benzene and its liquid halogenated derivatives. 2-Chloro-, 4-chloro-, 4,4'-dichlorobiphenyl and other isomeric dichloro- compounds were formed. The use of iron as a catalyst and highly chlorinated biphenyl as the solvent has been proposed.<sup>146</sup>

When the chlorine content of the product from chlorination of technical biphenyl reaches about 68 per cent, the material (which up to this point has remained a viscous liquid) suddenly becomes crystalline. The softening points of the chlorinated biphenyl mixtures which contain less than 68 per cent chlorine are rather low, usually below 64°C. In order to keep the higher-chlorinated biphenyls in a permanently stable, non-crystalline, solid state and to raise the softening point of the chlorinated biphenyl mixture, various percentages of the high-boiling compounds which are formed in the thermal synthesis of biphenyl are added to the crude biphenyl. In the accompanying graph (Fig. 149) there is shown the effect, according to Jenkins,<sup>147</sup> of different proportions of the high-boiling constituents on

<sup>144</sup> British P. 360,840, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1014. French P. 716,261, 1931; *Chem. Abs.*, 1932, 26, 2200.

<sup>145</sup> E. C. Britton and W. C. Stoesser, U. S. P. 1,835,754, Dec. 8, 1931, to Dow Chemical Co.; *Brit. Chem. Abs.* B, 1932, 220.

<sup>146</sup> J. E. Malowan, U. S. P. 1,951,577, Mar. 20, 1934, to Swann Research, Inc.; *Brit. Chem. Abs.* B, 1935, 93.

<sup>147</sup> R. L. Jenkins, U. S. P. 1,892,393, Dec. 27, 1932, to Swann Research, Inc.; *Chem. Abs.*, 1933, 27, 2032. British P. 358,704, 1930, to Federal Phosphorus Co.; *Chem. Abs.*, 1932, 26, 6165. French P.

the softening point and the crystallizing tendency. The curve *C* which refers to pure biphenyl could not be carried to higher softening points because of tendency to crystallize. By chlorinating the high-boiling compounds alone, still higher softening points may be obtained. One sample of such a mixture, reported by Jenkins, had 63.9 per cent chlorine and a softening point of 125.5°C.

In order to increase the proportion of complex, high-boiling constituents formed in the thermal synthesis of biphenyl, Durgin and Jenkins<sup>140</sup> increased the tempera-

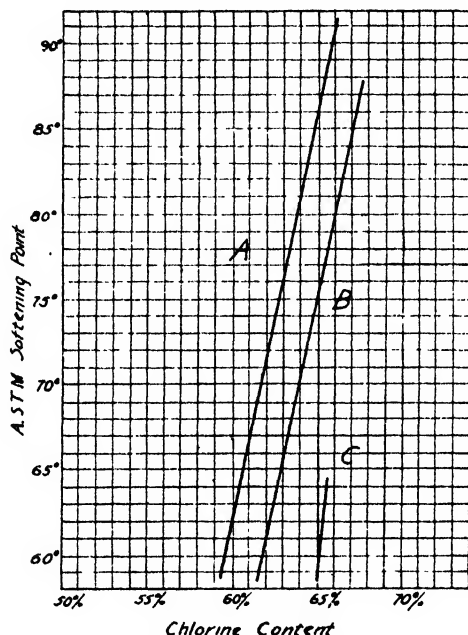


FIG. 149.—Softening Point as a Function of the Chlorination of (A) 60 per cent Biphenyl and 40 per cent High-Boiling Polyphenyls, (B) 80 per cent Biphenyl and 20 per cent High-Boiling Compounds and (C) 100 per cent Biphenyl. (R. L. Jenkins.)

ture of the bath of molten liquid and also used crude benzene. They state that when the reaction temperature is 750°C., the percentage of crude biphenyl, or the fraction boiling between 200° and 270°C., is approximately 4.5 per cent of the total condensate and that boiling about 270°C. is 0.4 per cent. By increasing the temperature to 850°C. the crude biphenyl fraction rises to approximately 15.5 per cent and the high-boiling to 5 per cent. If 90 per cent benzene is used in place of pure benzene and the temperature held at 850°C., the product, other than benzene, contains 30.5 per cent of the compounds boiling at 270°C.

In the presence of iron or nickel, the product of chlorination is colored. To obtain a clear, transparent product, Jenkins and Sikarski suggested iodine as a catalyst. For example, 60 g. of biphenyl and 40 g. of the high-boiling biaryl mixture were chlorinated. At the start 0.04 g. of iodine was added; and, as this was volatilized, additional 0.04 g. lots were added until a total of 0.4 g. was reached.

702,593, 1930; *Chem. Abs.*, 1931, 25, 4422. W. A. Cook and K. H. Cook (*J.A.C.S.*, 1933, 55, 1212) have studied the halogenation of *m*-diphenylbenzene.

<sup>140</sup> C. B. Durgin and R. L. Jenkins, U. S. P. 1,894,266, Jan. 17, 1933, to Swann Research, Inc.; *Chem. Abs.*, 1933, 27, 2459. For a description of these high-boiling substances, see W. A. Cook and K. H. Cook, *J.A.C.S.*, 1933, 55, 1212.



The temperature was held at 70°C. at the beginning of the reaction, but towards the end it was raised to 175-200°C.<sup>149</sup>

The same investigators distilled the initial products of chlorination and separated compounds having a wide range of softening points and varying from white to light yellow in color.<sup>150</sup> For example, molten, technical biphenyl was chlorinated until it had a specific gravity of 1.65 at 65°C. The product at this stage was a black solid having a chlorine content of approximately 63 per cent and an A.S.T.M. softening point of 50°C. This on distillation gave a soft, sticky wax having a Saybolt viscosity of 127 seconds at 210°F. When a mixture of biphenyl and 40 per cent of the higher biaryls was used, similar products were obtained. The softening points of the distillates in this case are shown in Figure 150.

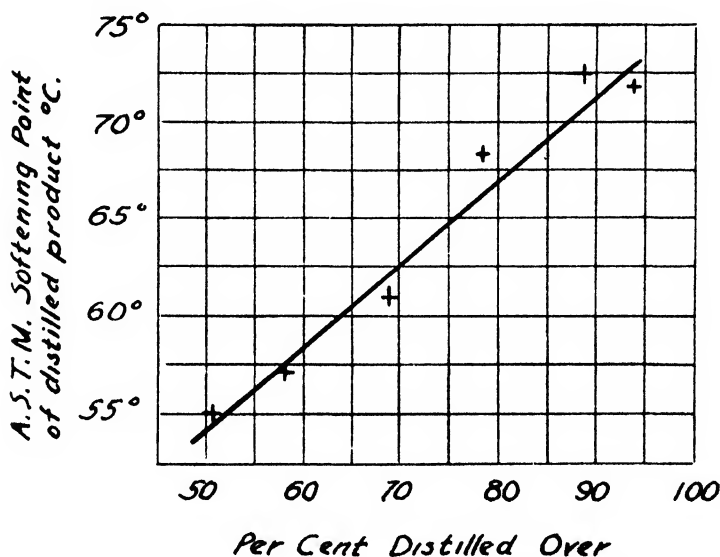


FIG. 150.—Softening Points of Chlorinated Biaryl Distillates. (R. L. Jenkins and J. A. Sikarski.)

**Properties and Uses of Chlorinated Biphenyl Resins.** These compounds have been produced commercially under the trade name "Aroclors."<sup>151</sup> The Aroclors range from a water-white, mobile oil to an amber-colored, transparent resin softening at 70°C. (see Fig. 151). The latter product is not combustible. Table 59 (on page 1146), which is abbreviated from one given by Penning,<sup>152</sup> gives the physical properties of some chlorinated biphenyl resins.

The Aroclors are soluble in a wide range of solvents. The principal ones in which they are insoluble or difficultly soluble are those which contain water or more than one hydroxyl group in the molecule, as for example, 95 per cent alcohol or glycerol.<sup>153</sup>

Aroclors are not hydrolyzed under ordinary conditions. Furthermore, they

<sup>149</sup> R. L. Jenkins and J. A. Sikarski, U. S. P. 1,892,399, Dec. 27, 1932, to Swann Research, Inc.; *Chem. Abs.*, 1933, 27, 2052.

<sup>150</sup> R. L. Jenkins and J. A. Sikarski, U. S. P. 1,892,400, Dec. 27, 1932, to Swann Research, Inc.; *Chem. Abs.*, 1933, 27, 2052. British P. 378,849, 1931, to Federal Phosphorus Co.; *Brit. Chem. Abs. B*, 1932, 998. French P. 715,074, 1931; *Chem. Abs.*, 1932, 26, 1811.

<sup>151</sup> *J.S.C.I.*, 1930, 49, 101.

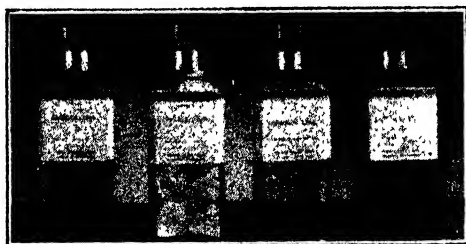
<sup>152</sup> C. H. Penning, *Ind. Eng. Chem.*, 1930, 22, 1180.

<sup>153</sup> R. L. Jenkins and R. N. Foster, *Ind. Eng. Chem.*, 1931, 23, 1362.

TABLE 59.—Physical Properties of Some Chlorinated Biphenyl Resins.

Property	Aroclor 1219	Aroclor 1242	Aroclor 1262	Aroclor 4465
Appearance.....	Water-white liquid	Water-white liquid	Light yellow, waxy resin	Pale amber resin
Melting or Softening point	14°C.	Liquid at 0°C.	Brittle resin at 0°C.	70°C.
Distillation range.....	278-295°C.	320-360°C.	374-410°C.	240-290°C. (9 mm.)
Specific gravity.....	1.1567 (25°/25°C.)	1.36 (65°/65°C.)	1.64 (65°/65°C.)	1.7 (25°/25°C.)
Viscosity, seconds Saybolt at 210°F.	30	34	96	Solid
Flash point.....	127°C.	174-178°C.	221°C.	257°C.
Flame point.....	176°C.	224°C.	None below boiling	492°C.
Refractive index.....	1.6125	1.6248	1.6493	

may be boiled with 10 per cent sodium hydroxide solution with no change. They are thermoplastic and nondrying, i.e., do not polymerize or oxidize on standing. They may be heated indefinitely at 150°C. and for short periods at higher temperatures with no apparent change. The light oils can be distilled at atmospheric pressure, and under vacuum the viscous oils and the solids can also be distilled. They have low vaporization losses. For the solids at 66°C., it is less than 0.04 g. per square inch per month.



Courtesy Monsanto Chemical Co.

FIG. 151.—Various Grades of Aroclors.

**Chlorinated Biphenyls in Varnishes and Dressings.** The viscous Aroclors are soluble in linseed and tung oils and may be employed as resins or gums in varnishes, particularly those of the short oil type in which cracking is due to the presence of brittle resins.<sup>134</sup> Varnishes made from the Aroclors are reported to be resistant to water and alkalis and partially so to flames. Gardner<sup>135</sup> prepared quick-drying varnishes and lacquers using chlorinated biphenyls mixed with other resins and oils. For example, 25 parts of chlorinated biphenyl were added at a temperature not above 190°C. to 132 parts of glycerol phthalate. Then 100 parts of this mixture were boiled with 200 parts of tung oil until a homogeneous composition was formed. This was thinned with turpentine before use. Gardner found that in this way he could produce a tough, light-colored film.

Although the lower chlorination products of biphenyl will burn, the higher derivatives do not and so may be used for flame-proofing purposes. According

<sup>134</sup> C. H. Penning, *loc. cit.* R. L. Jenkins, U. S. P. 1,974,801, Sept. 25, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, 28, 7562. L. D. Gittings (U. S. P. 1,974,799, Sept. 25, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, 28, 7553) has proposed a chlorinated biphenyl having approximately the formula  $C_{12}H_7Cl_5$  as a pigment with tung oil for a varnish.

<sup>135</sup> H. A. Gardner, U. S. P. 1,937,678, Nov. 15, 1932; *Chem. Abs.*, 1933, 27, 1530. British P. 351,637, 1930; *Chem. Abs.*, 1932, 26, 3125. German P. 563,080, 1930; *Chem. Abs.*, 1933, 27, 1539.

to Penning,<sup>126</sup> a practically fireproof material can be obtained by impregnation of wood with certain of the Aroclors, but the cost is considerably greater than when mineral salts are used. It is stated that the treated wood, however, instead of being brittle and lifeless, as is the case with the mineral-salts process, gains in strength. Impregnation of wood, fabric and paper with polychlorinated naphthalenes or biphenyls has been investigated by Engelhardt.<sup>127</sup> The latter substances mixed with ceresin and aluminum stearate are proposed also as agents to render textiles waterproof and fire-resistant.<sup>128</sup>

Darrin<sup>129</sup> used chlorine-substituted products of biphenyl as introfiers for the introduction of sulphur into the pores of paper, wood and ceramics. For example, 35 parts of sulphur were fused with 65 parts of resinous chlorobiphenyls. Paper material could be impregnated by dipping into the molten material, or if only a surface coating was desired, the mixtures could be sprayed or brushed on. The result was a hard, resistant, impervious, fireproof substance. Addition of selenium to the sulphur-chlorinated-biphenyl mixture increased protection against fire. For example, a composition of 40 parts of chlorinated biphenyls, 100 parts of sulphur and 15 parts of selenium exhibited as good a fireproofing quality and was much harder than one of 100 parts of sulphur and 200 parts of chlorinated biphenyls.<sup>130</sup>

Powdered sulphur coated with a fireproofing agent is prepared by spraying a mixture of molten sulphur and chlorinated biphenyl into a cooled atmosphere.<sup>131</sup> Sulphur so treated may be employed for impregnation of wood, porous pulp or paper. Gardner<sup>132</sup> employed a product obtained from heating sulphur with chlorinated biphenyl to assist the solution of heat-convertible phenol resins in drying oils.

Metal articles may be protected by coating with a layer of asphalt, then a layer of asbestos paper or felt saturated with a mixture of asphalt and chlorinated polyphenyl, and finally with a layer of asphalt.<sup>133</sup> Koch<sup>134</sup> used a solution of chlorinated rubber and chlorinated biphenyl in xylene or toluene to coat pipes which were to be buried underground.

Charch<sup>135</sup> employed as a moisture-proof, nontacky, flexible coating for sheets of regenerated cellulose, a composition made up of 1 part of chlorinated biphenyl, 0.33 part of a high-melting paraffin wax and 0.5 part of a plasticizer. Another suggested mixture consists of chlorinated polyphenyl (62.5 parts), dibutyl phthalate (5.4 parts) and finely ground silica (32.1 parts).<sup>136</sup>

According to Jenkins and Foster,<sup>137</sup> the Aroclors, although possessing both softening and resinous properties, are not to be regarded as exact substitutes for any of the present constituents of lacquers. In descending the series from the more viscous Aroclors to the less viscous, compatibility with nitrocellulose increases, as well as solubility in solvents. On the other hand with increase in viscosity,

<sup>126</sup> C. H. Penning, *loc. cit.*

<sup>127</sup> R. Engelhardt, German P. 567,261, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 27, 1479.

<sup>128</sup> C. L. Booth, U. S. P. 1,975,072, Oct. 2, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, 28, 7558.

<sup>129</sup> M. Darrin, U. S. P. 1,899,088, Nov. 29, 1932, 1,962,008, 1,962,004, June 6, 1934, and 1,994,810, Mar. 19, 1935, to F. N. Burt Co., Ltd.; *Chem. Abs.*, 1933, 27, 1511; 1934, 28, 4353; 1935, 29, 3076.

<sup>130</sup> M. Darrin, U. S. P. 1,962,008, June 6, 1934, to F. N. Burt Co., Ltd.; *Chem. Abs.*, 1934, 28, 4957.

<sup>131</sup> W. M. Kobbe, U. S. P. 1,833,818, Apr. 15, 1933, to Texas Gulf Sulphur Co.; *Brit. Chem. Abs.* B, 1933, 189. Sudden chilling of chlorinated biphenyl vapors, by a similar operation, yields a finely powdered material: R. S. Jenkins and T. W. Schib, U. S. P. 1,973,447, Sept. 4, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, 28, 6445.

<sup>132</sup> H. A. Gardner, U. S. P. 1,962,370, Feb. 26, 1935; *Chem. Abs.*, 1935, 29, 2764.

<sup>133</sup> J. H. Young, U. S. P. 1,812,733, June 30, 1931, to H. H. Robertson Co.; *Brit. Chem. Abs.* B, 1932, 351. British P. 371,683, 1931; *Chem. Abs.*, 1933, 27, 2308. See also U. S. P. 1,919,677, July 25, 1933; *Chem. Abs.*, 1933, 27, 4900.

<sup>134</sup> W. Koch, U. S. P. 1,950,894, Mar. 13, 1934, to Hercules Powder Co.; *Chem. Abs.*, 1934, 28, 3630.

<sup>135</sup> W. H. Charch, British P. 330,433, 1931, to Du Pont Cellophane Co., Inc.; *Brit. Chem. Abs.* B, 1932, 1641. See also R. L. Jenkins, U. S. P. 1,960,266, May 29, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, 28, 4600.

<sup>136</sup> R. L. Jenkins, U. S. P. 1,973,443, Sept. 4, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, 28, 6537.

<sup>137</sup> R. L. Jenkins and R. N. Foster, *Ind. Eng. Chem.*, 1931, 23, 1962. See also R. L. Jenkins, U. S. P. 1,942,926, Jan. 9, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, 28, 1890.

Aroclors have increased resistance to discoloration by sunlight; higher softening-, flash- and fire-points; less odor and volatility but a greater tendency to crystallize. For a lacquer, the choice of Aroclor depends on a balance of the above properties.

Jenkins and Foster made solutions of equal concentrations of Aroclors and 0.5-second nitrocellulose, mixing them in proportions to give a series of lacquers



*Courtesy Plastics Division, Carbide and Carbon Chemicals Corp.*

FIG. 152.—Raincoat Made from Plastic-Impregnated Cloth.

containing various ratios of the two. The appearance of the dried films indicated the limiting concentrations of the Aroclor, the films containing less than the limiting concentration being clear and those slightly more than the limit, opalescent by reflected light and brownish by transmitted light. These limiting concentrations are given in Table 60

TABLE 60.—Limiting Concentrations of Aroclors in Lacquers.

Aroclors		Nitrocellulose	
No.	Per Cent	Per Cent	Ratio
1242	50-60	50-40	About 1:1
1262	32	68	

Figures 153 and 154 are three-phase diagrams showing the compatibility of Aroclors with a few resins and  $\frac{1}{2}$ -second nitrocellulose. In the diagrams, the areas A, to the left and above each curve, include all those compositions of three nonvolatile components that give clear, unblushed films. The areas B, to the right

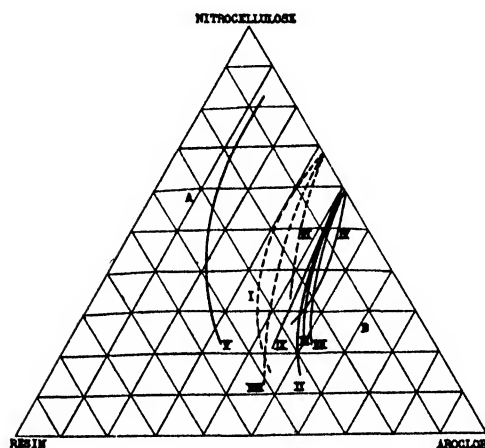


FIG. 153.

Courtesy Industrial and Engineering Chemistry

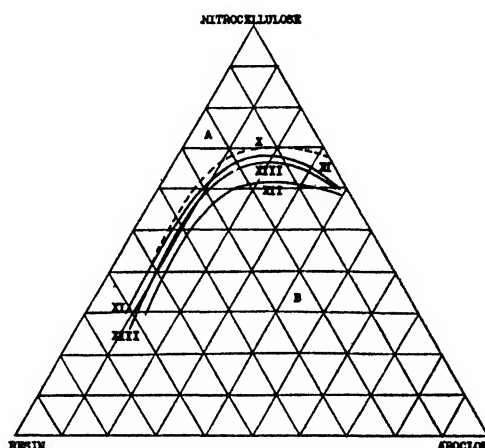


FIG. 154.

FIG. 153-154.—Compatibility of Aroclors with Resins and  $\frac{1}{2}$ -Second Nitrocellulose.  
(R. L. Jenkins and R. N. Foster.)

and down, give blushed films or ones that sweat. With the third components used in the systems plotted in Figure 153, there is an ample range of compatibility for the preparation of most types of varnishes. Those of Figure 154, on the other hand, require the addition of plasticizers.

The effect of different types of solvents on the compatible area is indicated by the curves. Keys to the resins and solvents studied are given in Tables 61 and 62 respectively.

TABLE 61.—Resins Employed in Compatibility Studies.

Curve	Resin	Aroclor	Solvent
I.....	Dammar	1262	1
II.....	Dammar	1254	1
III.....	Dammar	1254	2
IV.....	Rezyl-12	1254	1
V.....	Rezyl-12	1254	3
VI.....	Kopol-A	1262	1
VII.....	Kopol-A	1254	1
VIII.....	Glyptal-1202	1262	1
IX.....	Glyptal-1202	1254	1
X.....	Ester gum	1262	1
XI.....	Ester gum	1254	1
XII.....	Ester gum	1254	4
XIII.....	Amberol 200-B	1254	1

TABLE 62.—*Solvents Used in Studying Compatibility.*

Solvent	Composition
1	Technical amyl acetate.
2	50 parts toluene, 6.4 parts alcohol (specially denatured, formula 3-A), 6.4 parts butyl alcohol, 6.4 parts ethyl acetate, 30.8 parts butyl acetate.
3	70 parts toluene, 10 parts alcohol (specially denatured, formula 3-A), 10 parts ethyl acetate, 10 parts cellosolve.
4	65 parts toluene, 10 parts butyl alcohol, 25 parts butyl acetate.

Blom<sup>167</sup> has made a study of the effect of Aroclors on the mechanical properties of nitrocellulose films. It was found that the films showed increased breaking load and good elasticity and did not become brittle with additions up to 75 per cent of nitrocellulose. Castor oil was found to be an unsatisfactory plasticizer for nitrocellulose-Aroclor films because it tended to cause sweating.

The resinous Aroclors adhere strongly to glass and metal and it is said that joints between metal and glass surfaces are stronger than similar joints made with glue. However, the thermoplasticity of the resins is a disadvantage in this field. Gardner<sup>168</sup> reports that in making a shatterproof glass good adhesion is obtained when a chlorinated biphenyl resin is used in conjunction with a sheet of regenerated cellulose between the two glass plates. A cement consisting of resinous chlorobiphenyls and oxidized or polymerized oils has been used in the making of linoleum.<sup>169</sup> Jenkins prepared an odorless adhesive by chlorinating a mixture of polyphenyls.<sup>170</sup> Hetherington and Sim<sup>171</sup> also have made floor coverings from benzylcellulose, aromatic ethers of a polyhydric alcohol, fillers and chlorinated biphenyl or chlorinated naphthalene. It should be noted that chlorinated biphenyl has also been used as a plasticizer for benzylcellulose in lacquers.<sup>172</sup>

**Use of Molding and Insulating Compounds.** The thermoplastic properties of the Aroclors prevent their having more than restricted use as molding compounds. However, where it is desired to remelt and recast the compound, Aroclors have an advantage over natural waxes that on heating they are not altered in character through the loss of easily volatile constituents. Jenkins and Hardy<sup>173</sup> made a sealing wax from pine rosin and a biphenyl resin. For example, 100 parts of a black chlorinated biphenyl resin having a softening point of 72°C. were mixed with 100 parts of pine rosin and heated at 160°C. until a fluid product resulted. Two hundred parts of fine, red iron oxide were then stirred in. The melt was cast into molds.

The electrical properties of Aroclors are said to be very good, having a high dielectric constant and resistivity and a low power factor.<sup>174</sup> In fact, one of the principal outlets for the Aroclors has been in the electrical field. Thus, a dielectric material has been produced by Clark<sup>175</sup> by impregnating paper with halogenated aryl hydrocarbons such as a mixture of trichlorobenzene and hexachlorobiphenyl. Soda lime was included to absorb any hydrochloric acid evolved from the dielectric

<sup>167</sup> A. V. Blom, *Farben-Chem.*, 1933, 4, 244; *Brit. Chem. Abs. B*, 1933, 719.

<sup>168</sup> H. A. Gardner, U. S. P. 1,836,914, Dec. 15, 1931; *Chem. Abs.*, 1932, 26, 1087.

<sup>169</sup> H. A. Gardner, U. S. P. 1,831,707, Nov. 10, 1931; *Chem. Abs.*, 1932, 26, 861.

<sup>170</sup> R. L. Jenkins, U. S. P. 1,900,265, May 29, 1934, to Swann Research, Inc.; *Chem. Abs.*, 1934, 28, 4549.

<sup>171</sup> A. C. Hetherington and S. A. Sim, British P. 381,590, 1932, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 8585.

<sup>172</sup> L. Light, British P. 397,773, 1933; *Chem. Abs.*, 1934, 28, 1187.

<sup>173</sup> R. L. Jenkins and C. G. Hardy, U. S. P. 1,822,033, Sept. 8, 1931, to Swann Research, Inc.; *Brit. Chem. Abs. B*, 1933, 633.

<sup>174</sup> F. M. Clark, *Trans. Electrochem. Soc.*, 1934, 65, 193; *Brit. Chem. Abs. B*, 1934, 633. A. H. White and S. O. Morgan, *J. Franklin Inst.*, 1933, 216, 635; *Chem. Abs.*, 1934, 28, 1903.

<sup>175</sup> F. M. Clark, British P. 294,776, 1932, to Brit. Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1933, 717. French P. 41,743, 1933, and 43,663, 1934, addns. to 711,858, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1934, 28, 848; 1935, 29, 1533.

due to an arc discharge. Young<sup>176</sup> employed chlorinated biphenyl as an external coating of insulation on metal wire. An insulating composition has been made from chlorinated biphenyl by subjecting it to a high-tension electrical field and then purifying by distillation or filtration over Florida earth.<sup>177</sup> Another procedure is the chlorination of a mixture of biphenyl and other aromatic hydrocarbons (e.g., naphthalene) until the chlorine content reaches a value of 50-55 per cent.<sup>178</sup> A further proposed dielectric consists of a mixture of chlorinated biaryl and chlorinated olefin, e.g., dichlorostyrene.<sup>179</sup>

The use of a fluorinated aliphatic hydrocarbon, e.g., tetrachloro-difluoroethane, in amounts not exceeding 10 per cent of the total weight, with chlorinated biphenyl has been suggested.<sup>180</sup> The composition is improved by distilling in the presence of sodium or iron. The resulting liquid may be used for insulation purposes.

Chlorinated biphenyl may be employed in the manufacture of viscose yarns<sup>181</sup> as a delustering agent, in the preparation of soldering fluxes, particularly for aluminum alloys,<sup>182</sup> and in lithographic printing.<sup>183</sup>

**Chlorinated Naphthalenes.** Chloronaphthalenes in contrast to chlorobiphenyls are not strictly resins.<sup>184</sup> The products obtained from the various degrees of chlorination of naphthalene are wax-like and some of their components may be readily crystallized. According to Ellis,<sup>185</sup> naphthalene is easily chlorinated at 80°C. to about 45-50 per cent chlorine content. The solid material which separates from the naphthalene may be washed with alkali to remove free acid. Antimony chloride, phosphorus chlorides, sulphur and iodine are all catalysts for the reaction.<sup>186</sup> Control of the temperature during chlorination of molten naphthalene has been described by Engelhardt.<sup>187</sup> Payman and Gibson suggested ferric chloride as a catalyst for this reaction,<sup>188</sup> and the use of a solution of naphthalene in carbon tetrachloride at 5°C. with the same catalyst.<sup>189</sup> In both instances the products were distilled under reduced pressure. This method of purification was also used by Brown and Hanson, only they neutralized with lime or sodium hydroxide first.<sup>190</sup> Britton and Reed<sup>191</sup> have prepared chloronaphthalene in aromatic hydrocarbon solvents using iron as a catalyst.

The properties of the chlorinated naphthalenes have been investigated by

<sup>176</sup> J. H. Young, U. S. P. 1,863,147, June 14, 1931, to H. H. Robertson Co.; *Chem. Abs.*, 1932, 26, 4115. British P. 401,401, 1933; *Chem. Abs.*, 1934, 28, 2436.

<sup>177</sup> British P. 409,774, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1934, 587. French P. 745,480, 1933; *Chem. Abs.*, 1933, 27, 4325.

<sup>178</sup> F. C. Stephen, British P. 410,008, 1933, to Telegraph Condenser Co., Ltd.; *Chem. Abs.*, 1934, 28, 6218.

<sup>179</sup> French P. 774,693, 1934, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1935, 29, 2262.

<sup>180</sup> H. M. Elsey, U. S. P. 1,953,216, Apr. 3, 1934, to Westinghouse Elec. & Mfg. Co.; *Brit. Chem. Abs. B*, 1935, 30.

<sup>181</sup> French P. 738,966, 1932, to Viscose Co.; *Chem. Abs.*, 1933, 27, 2034. British P. 384,324, 1932; *Brit. Chem. Abs. B*, 1933, 103. British P. 409,521 and 409,525, 1933; *Brit. Chem. Abs. B*, 1934, 570.

<sup>182</sup> British P. 413,519, 1934, to Aluminum, Ltd.; *Chem. Abs.*, 1935, 29, 113.

<sup>183</sup> A. B. Poschel, British P. 393,132, 1933; *Chem. Abs.*, 1933, 27, 5553.

<sup>184</sup> For a review of the preparation, properties and uses of chloronaphthalene, see R. Strauss, *Chem.-Ztg.*, 1934, 58, 537.

<sup>185</sup> Carleton Ellis, U. S. P. 1,348,638, Dec. 4, 1917; *Chem. Abs.*, 1918, 12, 413.

<sup>186</sup> R. Engelhardt, German P. 548,360, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 2372. British P. 324,774, 1928; *Brit. Chem. Abs. B*, 1930, 410. French P. 667,024, 1929; *Chem. Abs.*, 1930, 24, 1135.

<sup>187</sup> R. Engelhardt, U. S. P. 1,933,422, Oct. 31, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 433.

<sup>188</sup> J. B. Payman and W. Gibson, British P. 291,849, 1927, to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1929, 23, 1139.

<sup>189</sup> J. B. Payman and W. Gibson, British P. 299,056, 1927, to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1929, 23, 1139. See also L. A. Levy and D. W. West, British P. 420,520, 1933; *Brit. Chem. Abs. B*, 1935, 140.

<sup>190</sup> S. Brown and E. R. Hanson, U. S. P. 1,953,070, April 3, 1934, to Halowax Corp.; *Brit. Chem. Abs. B*, 1935, 140. British P. 343,573, 1929; *Brit. Chem. Abs. B*, 1931, 668. French P. 682,508, 1929; *Chem. Abs.*, 1930, 24, 4533.

<sup>191</sup> E. C. Britton and W. R. Reed, U. S. P. 1,784,267, Dec. 9, 1930, to Dow Chemical Co.; *Chem. Abs.*, 1931, 25, 304.

Halls<sup>190</sup> who found that these waxes have a density of 1.5-1.7, a melting point range of 65-130°C. and a specific inductive capacity of 4.5-5.5. The compounds were relatively stable, although copper might be tarnished at 120-125°C., if water was present. It was also noted that the melting and boiling points of the chloronaphthalenes increase with the number of chlorine atoms in the molecule.

One of the principal industrial applications of the chloronaphthalene waxes has been in the field of insulating dielectrics.<sup>193</sup> In this connection their high specific inductive capacity is quite an advantage since this permits condensers to be made smaller than they can be when paraffin wax is used. Another advantage is the very slight change in volume in passing from a liquid to a solid. This reduces trouble due to the narrow channels in the dielectric left by solidification of the impregnating agent. There is a fairly linear relation between the capacity of condensers using chloronaphthalenes and the temperature. This facilitates the use and testing of the condensers. These waxes are good flame-proofing substances. It is stated that among the cautions which must be observed when using them are the avoidance of overheating or allowing air to come in contact with the molten mass and the rigid exclusion of water. They also are somewhat volatile and precautions should be taken to dispose of the fumes. Rücker has pointed out that the fumes have injurious effects on the skin. He obtained a refined product by blowing air through the crude chlorinated naphthalene while it is held at 215°C.<sup>194</sup> Others added alkaline substances to prevent irritant action on the skin.<sup>195</sup>

Aylsworth was one of the early investigators of chloronaphthalene insulating materials.<sup>196</sup> He noted that (for the same capacity) smaller condensers were required in which the chloro compounds were the dielectric, the slight effect of temperature on the capacity and the stabilizing action of distillation in the presence of a basic oxide.<sup>197</sup> Among the modifications he introduced was the oxidation of the chloronaphthalene waxes with air and nitric acid to increase the flexibility.<sup>198</sup> Incorporation of the resin from o-cresol and formaldehyde increased the dielectric strength of the chloro waxes.<sup>199</sup> Liquid or solid chloronaphthalenes are said to be useful as assistants in the vulcanization of rubber by sulphur. The resulting hard-rubber compositions were used as insulators or as chemically resistant coatings for metals.<sup>200</sup> Asphalt has been incorporated into these insulators by Edison;<sup>201</sup> while rubber, balata, gutta-percha and other natural and synthetic, oil-soluble resins have been used.<sup>202</sup> Condenser foils have also been manufactured by im-

<sup>190</sup> E. E. Halls, *Ind. Chemist*, 1933, 9, 58; *Chem. Abs.*, 1933, 27, 2631. See also V. Shvemberger and V. Gordan, *J. Gen. Chem. (U. S. S. R.)*, 1932, 2, 921; *Chem. Abs.*, 1933, 27, 2439.

<sup>191</sup> *Syn. Appl. Fin.*, 1933, 4, 143; *Brit. Chem. Abs. B*, 1933, 878. *Chem. Trade J.*, 1932, 91, 443; *Brit. Chem. Abs. B*, 1933, 189.

<sup>192</sup> K. Rücker, U. S. P. 1,455,509, May 15, 1923, to Chem. Foundation, Inc.; *Chem. Abs.*, 1923, 17, 2290. German P. 327,704, 1917, to Deutsche Konservierungsges.m.b.H.; *J.S.C.I.*, 1921, 40, 188A. The use of iron as a catalyst in the preparation of chloronaphthalenes reduces the quantity of low-boiling toxic constituents (German P. 332,725, 1920, addn. to 327,704, 1917, to Deutsche Konservierungsges.m.b.H.; *J.S.C.I.*, 1921, 40, 479A).

<sup>193</sup> British P. 309,421, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 590.

<sup>194</sup> J. W. Aylsworth, U. S. P. 914,323, March 2, 1909, to Fireproof Products Co.; *Chem. Abs.*, 1909, 3, 1446. U. S. P. 1,004,339, April 23, 1914, to Halogen Products Co.; *Chem. Abs.*, 1914, 8, 2119.

<sup>197</sup> J. W. Aylsworth, U. S. P. 1,111,289, Sept. 22, 1914, to Halogen Products Co.; *Chem. Abs.*, 1914, 8, 3536. U. S. P. 1,190,505, Aug. 29, 1916; *Chem. Abs.*, 1916, 10, 2625. See also S. Brown and E. R. Hanson, U. S. P. 1,933,070, April 3, 1934, to Halowax Corp.; *Chem. Abs.*, 1934, 28, 3745.

<sup>198</sup> J. W. Aylsworth, U. S. P. 1,133,423, May 16, 1916, to Halogen Products Co.; *Chem. Abs.*, 1916, 10, 1780.

<sup>199</sup> J. W. Aylsworth, U. S. P. 1,111,289, Sept. 22, 1914, *vide supra*.

<sup>200</sup> J. W. Aylsworth, U. S. P. 1,098,606, June 2, 1914, to Halogen Products Co.; *Chem. Abs.*, 1914, 8, 2314.

<sup>201</sup> T. A. Edison, U. S. P. 1,087,354, Jan. 6, 1914; *Chem. Abs.*, 1914, 8, 870.

<sup>202</sup> Allgem. Elektrizitäts-Ges., British P. 387,744, 1933, to International General Elec. Co.; *Chem. Abs.*, 1933, 27, 5847. A mixture of rosin, resin oil, chloronaphthalene and china clay has been used as a putty. C. W. Richards and H. Dodd, British P. 420,528, 1933, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1935, 163.



pregnating sheets with hot castor oil, followed by cooling in molten chlorinated naphthalene.<sup>303</sup>

It has been mentioned above that the chloronaphthalenes are flame-proofing substances.<sup>304</sup> They have been utilized for this purpose by Aylsworth,<sup>305</sup> Ellis<sup>306</sup> and Pyne and Parker.<sup>307</sup> Cloth previously impregnated with an inorganic salt, e.g., ammonium biphosphate, is rendered non-inflammable and waterproof by coating with a mixture of dichloronaphthalenes.<sup>308</sup> Tests on woods impregnated with chlorinated naphthalene indicated that it gave very good protection against insects and in addition stabilized the wood against warping due to changes in humidity.<sup>309</sup>

Engelhardt<sup>310</sup> suggests impregnation of bobbins (to be used in the wet treatment of textile threads) with chlorinated naphthalenes. Daniels<sup>311</sup> treated abrasive wheels (employed in contact with hot water) with a mixture consisting largely of penta-chloronaphthalene and solidifying at about 125°C. The higher chloro derivatives mixed with  $\alpha$ -chloronaphthalene give waterproof polishes.<sup>312</sup>

These products seem to adhere firmly to metallic surfaces and so have been used as coating compositions. The addition of sulphur<sup>313</sup> and other water-insoluble substances as talcum, barium sulphate and chromium sesquioxide<sup>314</sup> produces hard compositions. Delaney<sup>315</sup> mixed solid chloronaphthalene with an ester gum and about 5 per cent of rubber latex to form a cement for glass. Chlorinated naphthalenes have been used also in the preparation of sealing wax,<sup>316</sup> as a binding agent in the manufacture of laminated magnetic cores,<sup>317</sup> as a plasticizer for a silk solution,<sup>318</sup> dissolved in carbon tetrachloride and emulsified with water (using an emulsifying agent, e.g., Turkey-red oil) as an impregnating agent for textiles, an insecticide or a polishing material,<sup>319</sup> and to reduce the luster of rayon.<sup>320</sup>

Chloronaphthalene waxes have been suggested as substitutes for kauri gum and rosin,<sup>321</sup> or when mixed with gilsonite as a filling composition.<sup>322</sup> Chlorinated naphthalene in conjunction with stearic acid and inert materials (e.g., asbestos

<sup>303</sup> H. G. Ross, British P. 356,521, 1929, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1932, 26, 4000.

<sup>304</sup> Cf. A. W. C. Harrison, *Paint Manuf.*, 1932, 2, 103; *Chem. Abs.*, 1932, 26, 4967.

<sup>305</sup> J. W. Aylsworth, U. S. P. 914,222, March 2, 1909, to Fireproof Products Co., *Chem. Abs.*, 1909, 3, 1446.

<sup>306</sup> Carleton Ellis, U. S. P. 1,246,810, Nov. 13, 1917, to New Jersey Testing Laboratories; *Chem. Abs.*, 1918, 12, 298. U. S. P. 1,248,638, Dec. 4, 1917; *Chem. Abs.*, 1918, 12, 412.

<sup>307</sup> A. P. Pyne and T. B. Parker, British P. 400,235, 1933, to Johnson & Phillips, Ltd.; *Chem. Abs.*, 1934, 28, 2082.

<sup>308</sup> R. Engelhardt, U. S. P. 1,938,746, Dec. 12, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 1552.

<sup>309</sup> See *Syn. Appl. Fin.*, 1934, 5, 213; *Brit. Chem. Abs. B*, 1935, 109.

<sup>310</sup> R. Engelhardt, German P. 581,430, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5201. British P. 415,714, 1934; *Chem. Abs.*, 1935, 29, 943.

<sup>311</sup> R. S. Daniels, U. S. P. 1,900,430, Mar. 7, 1933, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 3053. British P. 318,017, 1928; *Chem. Abs.*, 1930, 24, 2549.

<sup>312</sup> J. B. Payman and W. Gibson, British P. 292,058, 1927, to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1929, 23, 1230. For the preparation of polishes and wax-like materials containing chloronaphthalenes, see W. Schrauth, U. S. P. 1,923,433, Sept. 26, 1933; *Chem. Abs.*, 1933, 27, 5000. See also British P. 342,737, 1929, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 4421. French P. 688,303, 1930; *Chem. Abs.*, 1931, 25, 833. C. W. Richards, British P. 406,355, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 4929.

<sup>313</sup> J. B. Payman and W. Gibson, British P. 292,057, 1927, to British Dyestuffs Corp., Ltd.; *Brit. Chem. Abs. B*, 1928, 597.

<sup>314</sup> British P. 338,904, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5908. French P. 737,329, 1932; *Chem. Abs.*, 1933, 27, 1730.

<sup>315</sup> M. E. Delaney, U. S. P. 1,945,803, Feb. 6, 1934, to Halowax Corp.; *Chem. Abs.*, 1934, 28, 2481. Also British P. 349,981, 1929, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 385. Canadian P. 310,617, 1931; *Chem. Abs.*, 1931, 25, 3137. French P. 691,293, 1930; *Chem. Abs.*, 1931, 25, 1046.

<sup>316</sup> E. R. Hanson and M. E. Delaney, U. S. P. 1,865,629, July 5, 1932, to Halowax Corp.; *Brit. Chem. Abs. B*, 1933, 399.

<sup>317</sup> H. Vogt, British P. 404,544, 1933; *Brit. Chem. Abs. B*, 1934, 356.

<sup>318</sup> I. Furman, British P. 418,303, 1934; *Chem. Abs.*, 1935, 29, 1543.

<sup>319</sup> C. W. Richards and H. Dodd, British P. 413,756, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1935, 29, 521. British P. 414,072, 1934; *Chem. Abs.*, 1935, 29, 251.

<sup>320</sup> F. D. Lewis, British P. 399,512, 1933; *Chem. Abs.*, 1934, 28, 1875. See also British P. 336,316, 1932, to Viscose Co.; *Brit. Chem. Abs. B*, 1933, 301. French P. 723,741, 1932; *Chem. Abs.*, 1933, 27, 3034.

<sup>321</sup> F. Frits, *Chem.-Ztg.*, 1933, 57, 997; *Chem. Abs.*, 1934, 28, 2923. K. Rucker, U. S. P. 1,455,506, May 15, 1933; *Chem. Abs.*, 1933, 17, 2290.

<sup>322</sup> French P. 691,394, 1930, to Bakelite Corp.; *Chem. Abs.*, 1931, 25, 1047.

or mica) may be molded into acid-proof vessels or floats for hydrometers.<sup>225</sup> Monochloronaphthalene is said to be a carbon remover for internal combustion engines.<sup>224</sup> Tetrachloronaphthalene is suggested for use in soldering as it is decomposed at soldering temperatures yielding hydrogen chloride.<sup>226</sup>

**Miscellaneous Resins by Halogenation.** In addition to the Aroclors and chloronaphthalenes, many other resinous bodies or amorphous compounds have been formed by chlorination of organic substances. In this section a few of these, together with their uses, will be given.

Sym-dichlorourea acts on phenol in alkaline aqueous solutions to form a tar.<sup>227</sup> Cresol, chlorocresol and their homologues, when treated with chlorine at temperatures above 100°C. until nearly free from substances volatile with steam, yield a hard, amorphous mass on cooling.<sup>227</sup> Tanaka, Morikawa and Sakamoto,<sup>228</sup> in attempting to prepare dichlorophenol derivatives for use as antiseptics, found that on passing chlorine into a mixture of 1,3,4-xylenol in carbon tetrachloride on ice, 2,6-dichloro-1,3,4-xylenol is obtained, but if the xylenol is chlorinated in the presence of phosphorus pentachloride at high temperatures a resinous substance is produced.

Tishchenko<sup>229</sup> studied the bromination of various phenols. The brominating agent employed was a solution of bromine in aqueous sodium carbonate. Quinol and pyrogallol were almost wholly resinified. Analogous experiments on  $\beta$ -naphthol using chlorine in place of bromine also gave a tar. Bromination of 1,1'-di- $\beta$ -naphthol is accompanied by the formation of resins.<sup>230</sup> Bromine water reacts with eugenol and isoeugenol to yield tarry materials.<sup>231</sup> The dimer of isoeugenol also is converted into a resin when chlorinated.<sup>232</sup> Meyer and Funke<sup>233</sup> reported that amorphous bodies resulted on treating o-cresolbenzoin with chlorine or iodine. The chlorination of o-benzyl alcohol disulphide led to the formation of a resin.<sup>234</sup>

Other compounds suggested as dielectrics or lubricants are the halogenated, phenyl derivatives of methane or ethane, e.g., chlorinated triphenylmethane and the chlorine derivatives of benzophenone.<sup>235</sup>

Paraffin, ceresin, montan wax, tung oil and petroleum can be chlorinated to a high degree by dissolving in carbon tetrachloride and introducing chlorine for a protracted period. The temperature may rise during the early stages of the reaction. After the temperature begins to fall the chlorination should be continued for some time. A transparent solid body is obtained from paraffin when the chlorine content reaches 70 per cent. Highly chlorinated paraffin is very resistant to acids and alkalies; it is not attacked by boiling 65 per cent nitric acid, concentrated hydrochloric acid or a 10 per cent aqueous solution of caustic soda. In spite of this resistance to strong reagents, there exists the tendency of chlorinated products of this character to split off hydrochloric acid on long standing. Chlorine is not so firmly united as it is in chloronaphthalene.<sup>236</sup>

<sup>225</sup> C. E. Lineberger, British P. 259,409, 1925; *Brit. Chem. Abs. B*, 1927, 2.

<sup>224</sup> C. A. Thomas and C. A. Hochwalt, U. S. P. 1,896,759, Feb. 7, 1933, to Thomas & Hochwalt Laboratories, Inc.; *Chem. Abs.*, 1933, 27, 2772.

<sup>226</sup> *Chem. Met. Eng.*, 1933, 40, 214.

<sup>227</sup> M. V. Likhoshervostov, *J. Russ. Phys.-Chem. Soc.*, 1929, 61, 1019; *Chem. Abs.*, 1930, 24, 836.

<sup>228</sup> German P. 355,173 and 355,174, 1920, to Chem. Fabr. vorm. Weiler-ter Meer; *J.S.C.I.*, 1922, 41, 772A.

<sup>229</sup> M. Tanaka, K. Morikawa and S. Sakamoto, *J. Chem. Soc. Japan*, 1930, 51, 275; *Chem. Abs.*, 1932, 26, 706.

<sup>230</sup> D. V. Tishchenko, *J. Russ. Phys.-Chem. Soc.*, 1928, 60, 153; *Chem. Abs.*, 1928, 22, 3397.

<sup>231</sup> G. Gallas and M. Alonso, *Anales soc. españ. ls. quim.*, 1930, 28, 967; *Brit. Chem. Abs. A*, 1930, 1875.

<sup>232</sup> J. Read and W. G. Reid, *J.C.S.*, 1928, 1487.

<sup>233</sup> E. Puzosdu, *Gazz. chim. ital.*, 1925, 55, 804; *Chem. Abs.*, 1926, 20, 747.

<sup>234</sup> R. Meyer and E. Funke, *Ber.*, 1924, 57, 1260; *Chem. Abs.*, 1925, 19, 371.

<sup>235</sup> A. Reimert and K. Crümer, *Ber.*, 1923, 61, 2563; *Chem. Abs.*, 1929, 23, 2163.

<sup>236</sup> French P. 770,845, 1934, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1935, 29, 814.

<sup>237</sup> German P. 345,779, 1910, to C. F. Boehringer & Söhne; *J.S.C.I.*, 1913, 31, 898. British P. 13,815, 1911; *J.S.C.I.*, 1913, 31, 1043. French P. 433,415, 1911; *J.S.C.I.*, 1913, 31, 390. M. Buchner, U. S. P.

Schaarschmidt<sup>287</sup> chlorinated molten paraffin above 150°C. until the chlorine content exceeded 61.4 per cent. At 150-160°C. a yellowish, transparent mass was obtained which if heated at 180-200°C. produced a brown, hard substance of high melting point. Free chlorine and hydrogen chloride were removed by passing air through the mass.

Geller<sup>288</sup> has investigated the use of chlorinated paraffin as a constituent of a synthetic chewing-gum base. In one experiment he mixed chloroparaffin resin with depolymerized crepe rubber. When heated, cooled and reheated, the rubber dissolved in the resin mixture which was then cooled and kneaded until a homogeneous mass was formed. Two and one-half parts of "hard" chloroparaffin resin, 1 part of "soft" chloroparaffin resin, 1 part of depolymerized rubber gave a "tough" base; 7 parts of hard paraffin resin, 7 parts of soft and 4 parts of depolymerized crepe rubber yielded a soft base. The hard chloroparaffin resin was made by treatment of paraffin (in carbon tetrachloride) with chlorine until it had about the physical characteristics of pine rosin. If chlorination is stopped when the fluid becomes thick then the soft form is obtained. Additional substances which Geller employed were stearin and calcium or magnesium stearate.

Groggins<sup>289</sup> investigated the chlorinated resins prepared by bubbling chlorine into p-cymene at temperatures above 25°C. Metallic aluminum, iron and zinc were used as catalysts. Chlorine substitution takes place in the side chains and the cymyl chlorides condense, splitting out hydrochloric acid. The reaction is catalyzed by the metallic chlorides formed by the action of hydrogen chloride on the particular metal used. The resins prepared in this manner contain 10-30 per cent chlorine. Groggins also formed resinous substances in a similar manner by chlorinating mixtures of p-cymene and other aromatic or aliphatic compounds. The resins were found to be insoluble in acids, alkalies and ethyl alcohol, but soluble in p-cymene, o-dichlorobenzene, turpentine, carbon disulphide and, to a lesser degree, in petroleum distillates. The resin solutions were recommended for use as lacquers or in treating railroad ties, telephone poles or marine piling.

In addition to chlorinated biphenyl and naphthalene resins, other chlorinated waxes or oils yield flame-proof, insulating materials.<sup>290</sup> Asphaltic oils, fish oils, waxes and coal-tar are employed for this purpose. Blakeman<sup>291</sup> treated drying oils, paraffin wax, naphthalene and various other raw materials with chlorine and introduced the chlorinated product into paints. A mixture of chlorinated asphaltum and chlorinated vegetable oil, the latter serving as a toughening agent, was employed by Wickenden<sup>292</sup> in paints and varnishes. For example, 10-20 per cent of cottonseed oil and petroleum asphaltum or pitch melting at 120°C. were mixed and chlorinated in a solution of carbon tetrachloride until the chlorination was complete. The solvent could be removed by distillation. A stable, highly chlorinated train oil for use as paint or binding agent was produced by treating exhaustively-chlorinated train oil with air or an inert gas until only a faint hydrogen-chloride reaction persisted. The temperature during the process could be raised to 70°C.<sup>293</sup> Air containing ammonia was then passed in and a small quantity of a difficultly volatile amine was added.

1,129,165, Feb. 23, 1915, to C. F. Boehringer & Söhne; *J.S.C.I.*, 1915, 34, 367. German P. 256,856, 1910 and 258,156, 1911; *J.S.C.I.*, 1913, 32, 499, 613. French P. 459,361, 1912; *J.S.C.I.*, 1913, 32, 1120. Catalysts are mentioned in German P. 275,165 and 275,166, 1912, addns. to 256,856, 1910; *Chem. Abs.*, 1914, 8, 3350.

<sup>287</sup> A. Schaarschmidt, German P. 442,890, 1920; *Brit. Chem. Abs. B*, 1923, 224.

<sup>288</sup> L. W. Geller, U. S. P. 1,855,016 and 1,855,017, Apr. 19, 1932, to American Chicle Co.; *Chem. Abs.*, 1932, 26, 3246.

<sup>289</sup> P. H. Groggins, *Ind. Eng. Chem.*, 1928, 20, 597. Cf. W. Quist, *Förh. III nord. Kemistmötet*, 1928, 194; *Brit. Chem. Abs. A*, 1929, 179.

<sup>290</sup> Carleton Ellis, U. S. P. 1,246,809 and 1,246,810, Nov. 13, 1917, to New Jersey Testing Laboratories; *Chem. Abs.*, 1918, 12, 298.

<sup>291</sup> W. N. Blakeman, Jr., U. S. P. 989,225, 989,226 and 989,227, Apr. 11, 1911; *Chem. Abs.*, 1911, 5, 2190.

<sup>292</sup> L. Wickenden, U. S. P. 1,393,094, Nov. 23, 1921; *Chem. Abs.*, 1923, 16, 843.

<sup>293</sup> British P. 223,801, 1926, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1930, 336.

Resinous materials may be obtained by chlorinating finely divided bituminous coal.<sup>344</sup> The method consists of passing chlorine through the powder or a suspension of it in a liquid and then extracting the product with a solvent. Finely divided lignite in the presence of water gives a resinous substance which may be used as a paint or a varnish.<sup>345</sup> Lignic acids give, on chlorination, resins which are soluble in acetone and amyl acetate. The films left by the evaporation of the solvent are hard, lustrous and tenacious.<sup>346</sup> The action of a solution of sodium hypochlorite saturated with chlorine on Cassel humic acid converts 70 per cent of it into a bright yellow humic acid which contains chlorine. The rest is highly polymerized.<sup>347</sup> In order to raise the softening point of coal-tar pitch, Balle chlorinated it at high temperatures in the presence of carriers.<sup>348</sup> The products were hard and lustrous. They had a conchoidal fracture and a softening point of 100-140°C. Zimmer<sup>349</sup> fused hexachloroethane and esters of fatty acids with tar or pitch in order to make a semi-fireproof coating. The adhesiveness of tar intended for road-making material is said to be increased by chlorination.<sup>350</sup>

Costeanu<sup>351</sup> has reported that when benzene and excess iodine were heated gradually to 600°C. in a sealed tube, a black, nacreous, infusible mass was formed. It had a composition corresponding to  $C_{10}H_{22}I$  and was not attacked by mineral acids. In the preparation of 3,5-di-iodo-4-hydroxydiphenyl sulphide, much tarry material was obtained when an aqueous ammonia solution of p-hydroxy-diphenyl sulphide was combined with an iodine solution.<sup>352</sup> The diazonium salt of the corresponding 2,6-di-iodo compound also gave an uncrystallizable substance when added to dilute sulphuric acid. Bromination of 9-benzylanthracene produced a resin,<sup>353</sup> and coating compositions which could be sprayed have been prepared by chlorinating m-styrene. In the latter case, the products with the largest content of chlorine have the lowest viscosities and the highest melting points.<sup>354</sup> 6,8-Tetradecadiyne, treated with bromine at room temperature, yields  $(C_6H_4CBr=CBr-)$ , with resinification. At 5°C. a yellow liquid is obtained which, on distillation, gives 1-bromoheptyne and a resin.<sup>355</sup> The formation of much tar was observed by Perkin and Stone<sup>356</sup> in the bromination of 2,4-dimethylbenzoyl bromide. They also report that addition of potassium cyanide to di(bromoethyl)benzoic acid furnished a small quantity of a red gum.

The fluorination of organic hydrocarbons has been studied by Bockemüller. Although in some cases he obtained fluoro compounds, in other instances resinification occurred. Resins also accompanied most of the identified products. As fluorinating agents he employed free fluorine,<sup>357</sup> lead tetrafluoride<sup>358</sup> and aryl iodide fluorides,  $R-IF_2$ .<sup>359</sup> Benzene, 1,1-diphenylethene, phenylethene, anthracene, phenanthrene and naphthalene were all found to give tars. The substituted compounds,

<sup>344</sup> A. McCulloch and A. Eccles, British P. 355,019, 1930; *Brit. Chem. Abs.* B, 1931, 1000.

<sup>345</sup> German P. 333,417, 1918, to Chem. Fabr. Griesheim-Elektron; *J.S.C.I.*, 1924, 43, 392B.

<sup>346</sup> C. S. Fuchs, German P. 314,418, 1918; *J.S.C.I.*, 1920, 39, 241A.

<sup>347</sup> W. Stengel, *Ges. Abhandl. Kenntnis Kohle*, 1930, 9, 125; *Chem. Abs.*, 1931, 25, 3808.

<sup>348</sup> G. Balle, German P. 406,889, 1922, to Farb- u. v. m. Meister, Lucius & Brünig; *J.S.C.I.*, 1925, 44, 199B.

<sup>349</sup> K. L. V. Zimmer, U. S. P. 1,084,520, Jan. 13, 1914; *Chem. Abs.*, 1914, 8, 1008.

<sup>350</sup> German P. 567,100, 1930, to Chem. Fab. Flörsheim H. Noerdlinger A.-G.; *Chem. Abs.*, 1933, 27, 1478.

<sup>351</sup> N. D. Costeanu, *Bull. soc. chim. Romania*, 1924, 6, 91; *Chem. Abs.*, 1925, 19, 1252.

<sup>352</sup> S. L. Base and T. B. Johnson, *J.A.C.S.*, 1930, 52, 1146.

<sup>353</sup> J. W. Cook, *J.C.S.*, 1926, 2166.

<sup>354</sup> H. B. Dykstra, U. S. P. 1,890,772, Dec. 13, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1933, 27, 1643. See also British P. 364,873, 1930, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1933, 27, 1643.

<sup>355</sup> V. Grignard and Tchoufaki, *Compt. rend.*, 1929, 188, 1531; *Chem. Abs.*, 1929, 23, 4439.

<sup>356</sup> W. H. Perkin, Jr. and J. F. S. Stone, *J.C.S.*, 1925, 127, 2295.

<sup>357</sup> W. Bockemüller, *Ann.*, 1933, 506, 20; *Brit. Chem. Abs.* A, 1933, 1139.

<sup>358</sup> O. Dimroth and W. Bockemüller, *Ber.*, 1931, 64, 516; *Chem. Abs.*, 1931, 25, 3642.

<sup>359</sup> W. Bockemüller, *Ber.*, 1931, 64, 522; *Chem. Abs.*, 1931, 25, 3642.

bromobenzene, m-dinitrobenzene, anisole, hydroquinone dimethyl ether and 3-phenylpropenoic acid behaved similarly.

Both bromo- and chloroanthraphenone resinify when boiled with a mixture of acetic and sulphuric acid.<sup>300</sup> Bromination of benzyl anthracene results in a resin as does the decomposition of benzyl dihydro-anthraquinyldipyridinium dibromide with water.<sup>301</sup>

Substances which may be utilized in the preparation of tanning agents were produced by chlorinating the black material obtained by steam-distillation of sulphuric acid sludge from the refining of benzene.<sup>302</sup> Highly chlorinated stable products which were considered as substitutes for natural resins or as tanning materials have been prepared from waste sulphite cellulose lye.<sup>303</sup> The waste

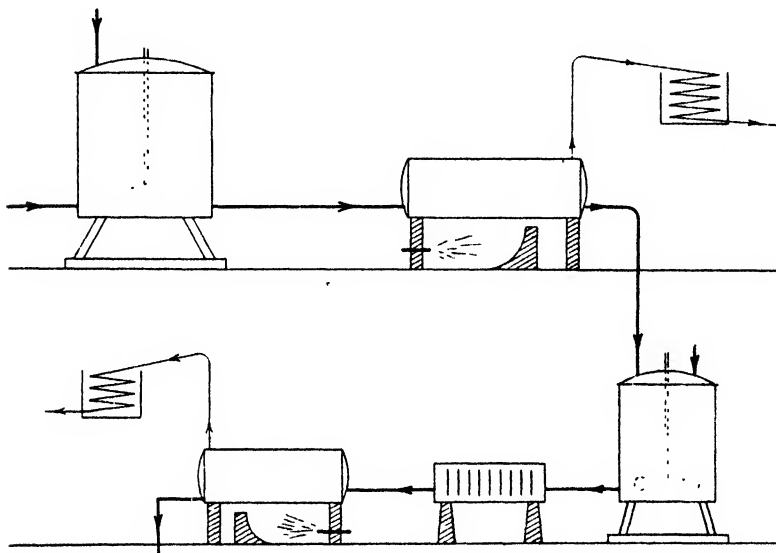


FIG. 155.—Flow Diagram for the Chlorination and Dechlorination of Cracked Petroleum Tar. (S. C. Fulton.)

liquor, evaporated without application of heat to a concentration of about 25 per cent, was treated while hot with chlorine gas for 2 hours. The resulting precipitate was separated and treated with a chlorate and hydrochloric acid. The product contained about 20 per cent chlorine.

A process for producing resins by chlorinating the polymeric constituents of cracked petroleum distillates has been developed by Morrell and Egloff.<sup>304</sup> Such constituents, after being separated from the distillates, were mixed with phenols, cresols, tar acids or other compounds, then heated to 300°F. and chlorine introduced until the mixture became relatively viscous.

According to Fulton,<sup>305</sup> a cracked petroleum fraction boiling between 300-660°F. (1 mm. pressure) may serve as the raw material for synthetic resins. (See Fig.

<sup>300</sup> J. W. Cook, *J.C.S.*, 1926, 1282.

<sup>301</sup> J. W. Cook, *J.C.S.*, 1926, 2170.

<sup>302</sup> German P. 403,647, 1921, to Koholyte-A.-G.; *J.S.C.I.*, 1925, 44, 369B.

<sup>303</sup> A. Schmidt, U. S. P. 1,567,395, Dec. 29, 1925; *Chem. Abs.*, 1926, 20, 666. British P. 178,104, 1922; *J.S.C.I.*, 1923, 42, 765A.

<sup>304</sup> J. C. Morrell and G. Egloff, U. S. P. 1,744,135, Jan. 31, 1930, to Universal Oil Products Co.; *Chem. Abs.*, 1930, 24, 1629.

<sup>305</sup> S. C. Fulton, U. S. P. 1,981,824, Nov. 20, 1934, to Standard Oil Development Company; *Chem. Abs.*, 1935, 29, 589.

155.) Chlorine is bubbled through the distillate, while it is agitated at room temperature, until 10-15 per cent is absorbed. Distillation of the product eliminates chlorine as hydrogen chloride and also any volatile oily constituents. Only traces of chlorine are found in the residue, which is dissolved in naphtha, filtered and the solvent evaporated. A lighter-colored resin may be obtained if the solution is treated with sulphuric acid and neutralized before removal of the solvent.

When added in amounts as low as 0.5 per cent the following substances are said to improve the film strength of hydrocarbon oils: the chlorinated derivative of stearic acid and diphenylene oxide, the product from chlorinated lard oil and naphthalene, condensate of 2 halogenated fatty acids or esters or of chlorinated stearic acid and chlorinated paraffin, halogenated diphenylene oxide, chlorinated ethyl oleate, and the condensation product of chlorinated wax with sodium ethoxide.<sup>300</sup>

Keller and Münz<sup>307</sup> have produced compounds which ranged from a viscous oil to plastic materials, and which were said to be colorless and sticky, by chlorinating or brominating fatty acids. Among the acids used by them were ricinoleic, oleic, stearic and dihydroxystearic acids. Pungs<sup>300</sup> suggested chlorination of oxidized paraffin. The resin so obtained was hard, flexible and yellow, with a chlorine content of 55 per cent. It could be further hardened by heating at 110°C.

In order to resolve (break) mineral oil emulsions, Lerch<sup>300</sup> used the reaction product of sulphonated cottonseed oil with a chlorination product of the polyolefin, cyclopentene or cyclohexene series.

A waterproof coating composition may be prepared by dissolving chlorinated wax (containing less than 30 per cent chlorine) in a solvent, e.g., turpentine or solvent naphtha.<sup>370</sup> Incorporation of other materials, for example ceresin or lamp-black, renders the coating capable of taking a high polish.

By removing halogen atoms from halogenated paraffin through heating with aqueous alkalis, various lubricating oils and tallowy substances may be produced.<sup>371</sup> The products contain halogen and hydroxyl groups as well as unsaturated linkages. If more than 9 halogen atoms are in the original molecule, based on an average molecular weight of 367, they may be removed by heating in an autoclave for 10 hours at 150-160°C. The product is a drying oil.<sup>372</sup> Rebs has made a pitch by a similar method.<sup>373</sup> Diphenylmethyl ethyl ether, obtained by refluxing diphenylchloromethane with ethyl alcohol, reacts with hydrogen chloride giving a considerable quantity of dark brown gum.<sup>374</sup> Similar products were found when sym-tetraphenyldimethyl ether was boiled with hydrochloric acid.

One of the compounds formed by treatment of 1,4-diphenyl-2-butyne-1,4-diol

<sup>300</sup> A. Henriksen and B. H. Lincoln, U. S. P. 1,939,979, Dec. 19, 1933, to Continental Oil Co.; *Chem. Abs.*, 1934, 28, 1524. French P. 761,243, 1934; *Chem. Abs.*, 1934, 28, 4220. U. S. P. 1,939,993, 1,939,994 and 1,939,995, Dec. 19, 1933; *Chem. Abs.*, 1934, 28, 1524. U. S. P. 1,936,670, Nov. 28, 1933; *Chem. Abs.*, 1934, 28, 1182. U. S. P. 1,944,941, Jan. 30, 1934; *Chem. Abs.*, 1934, 28, 2519. U. S. P. 1,945,615, Feb. 6, 1934; *Chem. Abs.*, 1934, 28, 3520.

<sup>307</sup> K. Keller and F. Münz, U. S. P. 1,862,596, June 14, 1932, to General Aniline Works; *Chem. Abs.*, 1932, 26, 4184.

<sup>300</sup> W. Pungs, German P. 451,116, 1923, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 28.

<sup>370</sup> W. B. Lerch, U. S. P. 1,890,789, Dec. 13, 1932, to Curo Process Co.; *Chem. Abs.*, 1933, 27, 1744.

<sup>371</sup> C. S. Schmidt, British P. 189,104, 1923, to A. Schmidt; *J.S.C.I.*, 1924, 43, 265B.

<sup>372</sup> British P. 243,948, 1929 and 367,545, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 578; 1932, 589. See also German P. 349,794, 1914, to Akt.-Ges. f. Anilin-Fabr., addn. to 281,175, 1913; *J.S.C.I.*, 1922, 41, 687A for the preparation of halogenated phenols from polyhalogenated aromatic hydrocarbons.

<sup>373</sup> British P. 372,784, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 714. See also E. Bielous, U. S. P. 1,884,423, July 12, 1931, to H. A. Gardner; *J.S.C.I.*, 1921, 40, 666A. H. A. Gardner and E. Bielous, *Ind. Eng. Chem.*, 1923, 14, 619. U. S. P. 1,884,447, July 12, 1931; *J.S.C.I.*, 1921, 40, 667A. Other methods for the preparation of drying oils from chlorinated hydrocarbons are discussed in Chapter 10. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc., New York, 1924.

<sup>374</sup> H. Rebs, German P. 343,466, 1915; *J.S.C.I.*, 1922, 41, 110A.

<sup>374</sup> A. M. Ward, *J.C.S.*, 1927, 2285.

with hydrogen bromide was a dibromide,  $C_{12}H_{12}Br_2$ . The latter reacts with alcoholic potassium hydroxide to yield a brown amorphous mass.<sup>276</sup> Similarly, the reaction between 2,5-dimethyl-2,5-hexen-diol and aqueous hydrobromic acid gives largely a dibromide which resinifies easily.<sup>276</sup>

The halogen derivatives of penthiazoline-2-dimethylmalonate and penthiazoline-2-acetic acid are slowly decomposed by hot water, with the formation of gums.<sup>277</sup>

<sup>276</sup> J. Salkind and A. Kruglov, *Ber.*, 1926, 59, 1936.

<sup>276</sup> J. Salkind and S. Sabolev, *Ber.*, 1929, 62, 2169.

<sup>277</sup> D. Worrall, *J.A.C.S.*, 1932, 54, 2061.

## Chapter 57

### Plastic Sulphur

Elemental sulphur possesses properties which closely resemble those of resins and has been used as a binder in molded products. Although this use of sulphur has not been as important as that of many other materials, yet the possibilities of its development warrant its inclusion here.

Sulphur is chemically different from synthetic resins, but its hardness, vitreous fracture and melting point cause it to resemble them rather closely. At normal temperatures and pressures, sulphur crystallizes in the rhombic system. At 95.4°C., this rhombic form is in equilibrium at atmospheric pressure with a monoclinic modification. With the absorption of something over 100 cal. of heat for each 32 g., rhombic sulphur is converted into the monoclinic.<sup>1</sup> Both of these crystalline modifications<sup>2</sup> have a molecular weight corresponding to  $S_8$ . Above the melting point, as the temperature rises, an amorphous sulphur ( $S_\mu$ ) is formed, and the liquid which was originally yellow increases in viscosity and darkens in color. The maximum viscosity is reached in the neighborhood of 200°C. The change from liquid sulphur to amorphous or plastic sulphur begins at about 160°C., however, the transition point can be substantially raised by the addition of foreign substances. Triphenylmethane, for instance, raises the transition point to 200°C.<sup>3</sup>

The accompanying graph of the viscosity of molten sulphur (on a semi-logarithmic scale) shows the change of this property with change of temperature (see Fig. 156). Presumably the course of the curve is profoundly influenced by polymerization of the element. The data<sup>4</sup> are dependent on the time of heating and the amount of gas or other impurities included in the sample. Hence the curve may not be strictly accurate.

Elemental sulphur in massive form has a marked resistance to acids, to oxidation and to weathering influences. Its hardness ranges from about 1.5 to 2.5 (Mohr scale), and its melting point is high enough to make it useful for many purposes. It possesses fairly good electrical and thermal insulating qualities.

Sulphur may be colored<sup>5</sup> red or brown and when so colored very closely resembles some resins. Colored sulphur castings have been prepared by heating

<sup>1</sup> R. Abegg, F. Auerbach and I. Koppel ("Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, 1927, IV (1), 152) give 3.13 cal. per g. From the equations of G. N. Lewis and M. Randall (*J.A.C.S.*, 1914, 36, 2469) the value calculated is 105+ cal. per gram-atom.

<sup>2</sup> Various modifications of the related element selenium have been obtained by S. Astin, A. C. C. Newman and H. L. Riley (*J.C.S.*, 1933, 391). More complete information on the forms of selenium is found in R. Abegg, F. Auerbach and I. Koppel, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, 1927, IV (1), 1, 693.

<sup>3</sup> P. Mondain-Monval and P. Schneider, *Compt. rend.*, 1928, 186, 751; *Chem. Abs.*, 1928, 22, 2299. *Bull. soc. chim.*, 1928, 43, 1302; *Chem. Abs.*, 1929, 23, 2614. The pseudo-ternary systems containing sulphur and quinoline, pyridine and p-xylene have been investigated by D. L. Hammick and W. E. Holt (*J.C.S.*, 1926, 1935).

<sup>4</sup> B. C. Farr and D. B. MacLeod, *Proc. Roy. Soc. London (A)*, 1920, 97, 80; *Chem. Abs.*, 1920, 14, 1916; L. Rotinjans, *Z. phys. Chem.*, 1908, 62, 609.

<sup>5</sup> W. H. Kobbe, U. S. P. 1,655,504, Jan. 10, 1928, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1928, 22, 1050. D. Finley, U. S. P. 1,803,008, April 21, 1931, to the Paraffine Co., Inc.; *Chem. Abs.*, 1931, 25, 8459. German P. 466,922, 1927, to Kunststein-Ind. W. Henker & Co. G.m.b.H.; *Chem. Abs.*, 1929, 23, 497. German P. 525,994, 1930, to Synthesit-Marmor-G.m.b.H.; *Chem. Abs.*, 1931, 25, 4682.



sulphur with any suitable addition substance to about 300°C., cooling the mixture to a casting temperature of 140-180°C., adding the coloring matter and then casting in the usual manner.<sup>6</sup> Sulphur as mined often contains a small amount of organic impurities which discolor it so that it may be almost any shade from light yellow to dark brown.<sup>7</sup> Kobbe<sup>8</sup> suggests the use of a variety of sulphur-soluble azo dyes for coloring sulphur orange, brown, red, green and black.

Because of its tendency to crystallize, untreated sulphur has very little prospective value in liquid coating compositions. That is, a solution of sulphur when

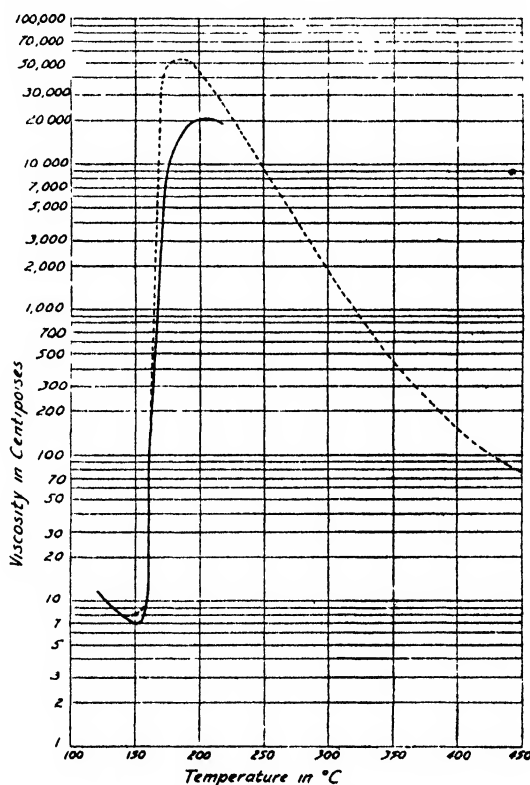


FIG. 156.—Change in Viscosity of Sulphur with Temperature. Dotted line represents data by L. Rotinjanz (*Z. physik. Chem.*, 1908, 62, 609) and solid line data by C. C. Farr and D. B. Macleod, *Proc. Roy. Soc. (London)* A, 1920, 97, 80.

applied with a brush to a surface and allowed to dry forms a crystalline coating of no particular value. Also, if applied to metals or to other materials which are readily affected by acids, the coating may have a deleterious effect because of the possibility of acids forming by its oxidation. Although finely ground sulphur is practically unaffected by air<sup>9</sup> at 60-80°C., flowers of sulphur are readily oxidized at even lower temperatures. However, these two forms of sulphur have been used in paints and varnishes to cover surfaces with anti-fouling or antiseptic

<sup>6</sup> P. Scholz, German P. 436,170, 1924; *Brit. Chem. Abs.* B, 1927, 482.

<sup>7</sup> J. W. Schwab, U. S. P. 1,656,504 and 1,656,505, Jan. 17, 1928; 1,683,731, Sept. 11, 1928; 1,692,422, Nov. 20, 1928, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1928, 22, 1019, 4313; 1929, 23, 677.

<sup>8</sup> W. H. Kobbe, *loc. cit.*

<sup>9</sup> J. E. Stephenson and S. W. Bridge, *Analyst*, 1929, 54, 590, 787; *Chem. Abs.*, 1930, 24, 33, 1049.

coatings.<sup>10</sup> Furthermore, it has been stated that 40 parts of cement, 5 parts of mica, and 5 parts of aluminum in 50 parts of molten sulphur give an acid-resisting surface.<sup>11</sup> Another coating which has been suggested consists of a mixture of sulphur and pitch.<sup>12</sup>

Elemental sulphur has certain fields of application which appear to be promising. However, its use is restricted because its desirable properties are offset by its brittleness and its tendency to crystallize. Plastic sulphur holds promise of greater usefulness than crystalline sulphur, since it is somewhat similar to rubber. Trillat and Forestier<sup>13</sup> have shown that plastic sulphur, prepared by heating sulphur to a temperature above 230°C. and then pouring it into cold water, stretches upon rapid drawing to a permanent lengthening of 800-1000 per cent and, at the same time, its physical properties such as transparency and elasticity are changed. The sulphur was amorphous before drawing and crystalline afterward, but the crystalline structure was not the same as that of ordinary orthorhombic sulphur. They have also shown that x-rays stimulate the recrystallization of plastic sulphur. The stress-strain curves for thin filaments of plastic sulphur and of raw rubber have been determined by Strong,<sup>14</sup> and there is some similarity between the two series of curves. Hammick and Zvegintsov<sup>15</sup> suggested that amorphous sulphur is a gel and confirmed this view by observing the Tyndall effect in pure molten sulphur. Like many other substances, if plastic sulphur is kept at a sufficiently low temperature it will not crystallize. Mondain-Monval found that for sulphur this temperature was -29°C.<sup>16</sup>

Above 160°C., sulphur is stable in an amorphous form, mixed probably with small amounts of the two crystalline modifications. Sudden cooling yields a rubbery, elastic material which is unstable at ordinary temperatures and retains its elasticity normally for only a few hours after cooling below the transition temperature. The author has made a number of experiments on the problem of retaining sulphur in a plastic condition and believes that it will be possible to make use of sulphur in this form commercially. Although molten sulphur combines with many organic substances, the larger number of them are not readily soluble therein. The products made by treating phenol or its homologues with sulphur chloride<sup>17</sup> are among the few that dissolve readily in molten sulphur. These retard pronouncedly reversion from the plastic to the crystalline form.<sup>18</sup> Cumarone resin has also been used with sulphur to maintain it in a plastic condition. For example, Grant and Farren<sup>19</sup> employed cumarone resin and sulphur which had been fused together, either with or without a finely divided filler, as a sealing and insulating composition. They reported that the crystallization of sulphur in this mixture was completely prevented. Certain types of cumarone resin when used for rubber compounding cause "blooming" when the unvulcanized rubber stock is stored, but it has been found that<sup>20</sup> this difficulty can be minimized if from 15 to 20 per cent of sulphur is dissolved in the resin before compounding. The

<sup>10</sup> R. Bell, U. S. P. 817,743, Apr. 17, 1906. R. Weithöner, German P. 386,821, 1922, to Chem. Laboratorium für Anstrichstoffe G.m.b.H.; *J.S.C.I.*, 1924, 43, 392B.

<sup>11</sup> F. D. Sullivan, U. S. P. 1,808,981, June 2, 1931; *Chem. Abs.*, 1931, 25, 4372.

<sup>12</sup> J. J. White, U. S. P. 1,853,003, Sept. 14, 1920; *Chem. Abs.*, 1920, 14, 3509.

<sup>13</sup> J. J. Trillat and J. Forestier, *Compt. rend.*, 1931, 192, 559; *Chem. Abs.*, 1931, 25, 3215.

<sup>14</sup> J. D. Strong, *J. Phys. Chem.*, 1928, 32, 1225; *Brit. Chem. Abs. B*, 1928, 709.

<sup>15</sup> D. L. Hammick and M. Zvegintsov, *J.C.S.*, 1930, 273. Cf. B. Lange and W. Cousins, *Z. physik. Chem.*, Abt. A, 1929, 143, 135; *Chem. Abs.*, 1929, 23, 5363.

<sup>16</sup> P. Mondain-Monval, *Compt. rend.*, 1934, 198, 1413; *Brit. Chem. Abs. A*, 1934, 587.

<sup>17</sup> See Chapter 59.

<sup>18</sup> Carleton Ellis, U. S. P. 1,676,604, July 10, 1928; *Chem. Abs.*, 1928, 22, 3269. U. S. P. 1,835,767, Dec. 8, 1931; *Chem. Abs.*, 1932, 26, 1143. U. S. P. 1,690,335, Nov. 6, 1928; *Chem. Abs.*, 1929, 23, 533. U. S. P. 1,814,135, July 14, 1931; *Chem. Abs.*, 1931, 25, 5291. U. S. P. 1,835,766, Dec. 8, 1931; *Chem. Abs.*, 1932, 26, 1123.

<sup>19</sup> H. L. Grant and W. R. Farren, U. S. P. 1,612,576, Dec. 23, 1926, to Atlas Powder Co.; *Chem. Abs.*, 1927, 31, 617.

<sup>20</sup> S. F. Miller, U. S. P. 1,752,963, Nov. 25, 1929, to Barrett Co.; *Chem. Abs.*, 1931, 25, 487.

solubility of sulphur depends to some extent on the melting point of the resin. Endres<sup>21</sup> proposed a method of avoiding sulphur bloom in rubber compositions by using plastic sulphur in which the content of rhombic sulphur had been reduced to less than 1 per cent by extraction with carbon disulphide.

Deines believed that the only amorphous form is the solid sulphur which is insoluble in carbon disulphide. He reported that highly sulphurized hydrogen persulphides caused the earlier investigators to come to erroneous conclusions<sup>22</sup> as to the number of amorphous forms.

A stable form of plastic sulphur has been made by heating equal parts of sulphur and antimony trichloride to 400°C. under pressure and then rapidly cooling the melt by pouring it into cold water.<sup>23</sup> This product when mixed with wood tar, coal tar and paraffin wax served as a binder for molded electrical insulation. When approximately equal parts of sulphur and selenium are heated together above the melting point of selenium a cherry-red compound, selenium sulphide



<sup>21</sup> Courtesy Texas Gulf Sulphur Co.

FIG. 157.—Loading Sulphur from One of the Vats at the Texas Gulf Sulphur Company Mine.

is formed.<sup>24</sup> When cooled to room temperature this sulphide forms a black, elastic mass, which remains in the same condition for several days and which gradually becomes so hard and brittle that it may be ground to an orange-red powder melting at about 100°C. This change into a hard, brittle state takes place in about half an hour if the elastic mass is maintained at a temperature of 80-90°C. Nordlander believes that this sulphide in the elastic state is highly polymerized and that it becomes hard and brittle through depolymerization. Selenium sulphide, used as a binder in forming gears and similar products, possesses two noteworthy features. It is unaffected by water or by concentrated acids (excepting nitric acid), and, although it sets to a hard and dense material at 80-90°C., it will

<sup>21</sup> H. A. Endres, Canadian P. 323,078, 1932, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1932, 26, 4207. British P. 374,624, 1933; *Chem. Abs.*, 1933, 27, 3854.

<sup>22</sup> O. v. Deines, *Z. anorg. allgem. Chem.*, 1933, 213, 183; *Chem. Abs.*, 1933, 27, 5017.

<sup>23</sup> I. F. Slastikov, Russian P. 4799, 1928; *Chem. Abs.*, 1929, 23, 1191.

<sup>24</sup> B. W. Nordlander, U. S. P. 1,761,740, June 3, 1930, to General Electric Company; *Chem. Abs.*, 1930, 24, 3617. British P. 351,138, 1930, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1931, 853. Canadian P. 330,776, 1932, to Canadian General Electric Co.; *Chem. Abs.*, 1932, 26, 3833. For the use of this compound in vulcanising rubber, see B. W. Nordlander, U. S. P. 1,237,604, Oct. 13, 1931, to General Electric Co.; *Brit. Chem. Abs. B*, 1932, 682. French P. 668,110, 1933, to Compagnie française Thomson-Houston; *Chem. Abs.*, 1933, 24, 1546.

revert to the plastic state if heated to about 110°C. A sulphide exhibiting similar properties is obtained from tellurium.

Wax-like substances may be incorporated with sulphur to modify its properties. Chlorinated naphthalene,<sup>25</sup> for example, has been melted with sulphur to produce a hard and porcelain-like mixture. This mixture has good adherence when applied to metallic or other surfaces. A sulphur composition, made by blending a small proportion of sulphur with waxes or resins,<sup>26</sup> has been proposed as a binding agent in plastic compositions and as a floor wax. When 4 parts of dark-colored carnauba wax and 1 part of rosin are fused with 0.1 part of sulphur and then cooled, the product is light in color, opaque and without a prominent waxy appearance. If sulphur is omitted, the resulting material is dark in color and slightly translucent. Rosin esters when treated in a similar manner show an even more pronounced lightening in color due to the presence of the sulphur. On the other hand, the addition of 0.1-1.0 per cent of rosin to molten sulphur makes the product less liable to dust explosion on grinding, and the powdered mixture does not cake on standing, making it useful as an insecticide.<sup>27</sup> A mastic composition to be used in laying floor blocks has been prepared from a sulphur-rosin mixture containing 15-25 per cent of a lubricating oil.<sup>28</sup> A mixture of cashew nut-shell oil and sulphur has been suggested also as a plastic.<sup>29</sup>

A rubber-like material may be prepared in the following manner:<sup>30</sup> Equal parts of hardened rosin and boiled oil are heated together until the rosin is melted and thoroughly incorporated with the oil. An equal weight of sulphur balsam (consisting of 3 parts of boiled oil and 2 parts of sulphur) is added and the resulting mixture heated to 300°F. On cooling, an elastic product is obtained which may be employed as a waterproofing agent.

Myers<sup>30</sup> made a tough and non-brittle cement by mixing 1 or 2 grains of arsenic per lb. of sulphur. The mixture was applied while it was fluid and was especially designed to anchor a vitreous facing to brick or similar materials. Hamor and Duecker prepared relatively stable plastic sulphur by rapidly cooling a solution of phosphorus sulphide in sulphur from above 200°C. More than 10 per cent of phosphorus sulphide was used.<sup>31</sup> Arsenic and thallium, or their oxides or sulphides, also act as stabilizers.<sup>32</sup> Olefin polysulphides are said to exert a similar effect.<sup>33</sup>

The consideration of sulphur as a binding agent is a subject seemingly unrelated to synthetic resins. However, its cheapness coupled with its other desirable properties has led to its use in various ways where the cost of higher-priced, fusible binders is prohibitive. The addition of a number of materials (particularly chlorinated compounds) has been shown to retard or to prevent the burning of sulphur.<sup>34</sup>

The author has made various molded articles by hot pressing mixtures of

<sup>25</sup> J. B. Payman and W. Gibson, British P. 292,057, 1927, to British Dyestuffs Corp., Ltd.; *Chem. Abs.*, 1929, 23, 1229.

<sup>26</sup> Carleton Ellis, U. S. P. 1,815,615, July 21, 1931, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 5526.

<sup>27</sup> W. L. Wright, U. S. P. 1,935,466, Oct. 31, 1933, to Oswego Falls Corp.

<sup>28</sup> F. W. Wiedner, U. S. P. 1,908,619, Mar. 9, 1933, to San Francisco Sulphur Co.; *Chem. Abs.*, 1933, 27, 3772.

<sup>29</sup> H. C. Nielsen, U. S. P. 1,841,667, Jan. 19, 1932, to Nat. Wood Products Co.; *Brit. Chem. Abs. B*, 1932, 1043.

<sup>30</sup> M. T. Harvey, U. S. P. 1,838,071, Dec. 22, 1931, to Harvel Corp.; *Brit. Chem. Abs. B*, 1932, 902.

<sup>31</sup> A. K. Kissel, British P. 4918, 1896; *J.S.C.I.*, 1887, 6, 219.

<sup>32</sup> C. Myers, U. S. P. 624,523, May 9, 1899, to M. J. Murphy and H. Rosenbaum.

<sup>33</sup> W. A. Hamor and W. W. Duecker, U. S. P. 1,959,026, May 15, 1934, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1934, 28, 4547.

<sup>34</sup> W. A. Hamor and W. W. Duecker, U. S. P. 1,981,232, Nov. 20, 1934, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1935, 29, 522.

<sup>35</sup> W. W. Duecker, *Chem. Met. Eng.*, 1934, 11, 583. For a discussion of Thiokol, see Chapter 58.

<sup>36</sup> C. Marx, U. S. P. 1,619,557, Mar. 1, 1927, to Union Sulphur Co.; *Chem. Abs.*, 1927, 21, 1387. Carleton Ellis, U. S. P. 1,535,767, Dec. 8, 1931; *Chem. Abs.*, 1932, 26, 1143. W. H. Kobbe, U. S. P. 1,830,515, Apr. 12, 1932; *Chem. Abs.*, 1932, 26, 3542.

sulphur and fillers. Although these articles had neither the strength nor the surface finish common to resin-containing products, it was found that the compositions had little or no effect on steel molds. Prior to this investigation the criticism that sulphur would blacken the molds had been advanced.

Darrin and others have made a study of what he has termed introfiers or impregnation accelerators.<sup>55</sup> According to him, when an introfier is added it changes the fluidity and the wetting properties of the impregnating material and so increases the penetration. Introfaction cannot be attributed solely to a thinning action, since the amount of introfier required is often very small, and its mechanism is not understood. Darrin states that different classes of substances require different types of introfiers; for instance, a sulphur introfier must have a molecular structure which contains at least two benzene rings. Naphthalene and its derivatives are good sulphur introfiers, and biphenyl, benzyl ether and carbazole are reported to have been used with satisfactory results. The Aroclors are also suggested as introfiers. One difficulty which might be encountered in using them is their "chemical odor."

Some method similar to those which have been discussed for maintaining sulphur in the plastic form may lead to its more extensive use in molded articles as a binding agent where a certain degree of elasticity is required. Bleecker made an impervious, chemically-resistant material by using as a binder for inert fillers sulphur so finely crystalline as to be nearly amorphous. Artificial graphite, sand, coke and pulverized slate were some of the fillers employed.<sup>56</sup> He prevented the growth of large sulphur crystals by rapidly cooling the molten sulphur-filler mixture under pressure, and also by adding such substances as coal-tar pitch or analogous hydrocarbons which react with the molten sulphur. This material could be used in making pipe linings, conduits and machine parts. The products were impervious to liquids and gases and were highly resistant to the action of acids and other chemicals.

Wood has been preserved and strengthened by impregnation with a molten-sulphur solution of a toxic material, e.g., arsenic and phosphorus sulphides.<sup>57</sup> The use of sulphur-soluble, organic arsenic compounds is also recommended.

The art of molding sulphur goes back more than sixty years and from time to time has been commercially important. The cheapness and low melting point of this element, coupled with its hardness, resistance to corrosive action and water, and its electrical insulating value, have allowed it to occupy a not unimportant place in commerce. Brittleness coupled with a high coefficient of thermal expansion and its pronounced shrinkage on solidification have prevented its wider usefulness.

The applications in which its shortcomings are partially overcome may be divided into two principal groups: the manufacture of casting compositions formed by dilution with suitable materials, insoluble in molten sulphur, to overcome the high shrinkage and to bind the brittle sulphur crystals together; and the impregnation of porous materials with molten sulphur to increase their strength and reduce their porosity.

In casting or molding compositions containing sulphur, the more common

<sup>55</sup> M. Darrin, U. S. P. 1,644,711, Oct. 11, 1927, and 1,962,003, June 5, 1934, to F. N. Burt Co.; *Chem. Abs.*, 1927, 21, 4036; 1934, 28, 4858. U. S. Reissue 17,867, Nov. 11, 1930; *Brit. Chem. Abs. B*, 1931, 30. British P. 391,500, 1937; *Brit. Chem. Abs. B*, 1928, 657. German P. 559,302, 1927; *Chem. Abs.*, 1933, 27, 818. H. P. Munger, M. Darrin and G. Stegeman, *J. Phys. Chem.*, 1930, 34, 593; *Chem. Abs.*, 1930, 24, 3367. M. Darrin, *Ind. Eng. Chem.*, 1928, 20, 801. M. Darrin (U. S. P. 1,962,003, June 5, 1934, to F. N. Burt Co., Ltd.; *Chem. Abs.*, 1934, 28, 4857) has described the use of introfiers with mixtures of sulphur and selenium.

<sup>56</sup> W. P. Bleecker, U. S. P. 1,660,371, Feb. 28, 1928; *Chem. Abs.*, 1928, 22, 1447. U. S. P. 1,686,197, Oct. 2, 1928; *Chem. Abs.*, 1928, 22, 4740. U. S. P. 1,664,760, Dec. 11, 1928; *Chem. Abs.*, 1929, 23, 676.

<sup>57</sup> D. B. Bradner, U. S. P. 1,653,811, Dec. 18, 1927, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1928, 22, 559.

addition is carbon in the form of anthracite coal,<sup>33</sup> graphite<sup>34</sup> or coke,<sup>35</sup> either ground or reduced to colloidal particles.<sup>36</sup> Numerous inorganic fillers have been proposed, such as powdered metals,<sup>37</sup> steatite,<sup>38</sup> bentonite,<sup>39</sup> asbestos,<sup>40</sup> silica,<sup>41</sup> and a mixture of pumice, sand, magnesium carbonate and asbestos.<sup>42</sup> Sawdust,<sup>43</sup> dried powdered peat,<sup>44</sup> wood flour,<sup>45</sup> cassava starch,<sup>46</sup> casein<sup>47</sup> and refined cellulose<sup>48</sup> have been suggested as organic fillers.

As examples of the methods for preparing and casting sulphur compositions, mention may be made of those used by Kobbe<sup>49</sup> and Barnes.<sup>50</sup> The latter pulverized both sulphur and anthracite coal to impalpable powders. Ten parts of the pulverized sulphur were mixed with fifty of powdered coal and the mixture heated until it was fluid enough to pour. Kobbe recommended melting the sulphur and mechanically incorporating comminuted silica the grain size of which was not uniform, but varied as is shown by the following screen analysis (Table 63).

TABLE 63.—Screen Analysis of Silica.

	Per Cent
Held on 80 mesh.....	7.2
Passing 80 mesh, held on 100.....	5.6
Passing 100 mesh, held on 200.....	25.0
Passing 200 mesh, held on 320.....	19.0
Passing 320 mesh.....	43.2

He used approximately equal weights of silica and sulphur since this represented a good balance between too much silica with consequent lack of fluidity and too little silica with consequent lack of strength. The product was light in color and possessed a tensile strength of about 623 lbs. per square inch. The addition of alkali to the melt<sup>51</sup> and the use of aluminum molds<sup>52</sup> have been proposed as means of preventing the casting from sticking to the mold. These sulphur compositions have been molded into a variety of shapes, used as luting or sealing cements,<sup>53</sup> and applied on concrete to form a protective coat against acids.<sup>54</sup>

- <sup>33</sup> W. W. Barnes, U. S. P. 371,406, Oct. 11, 1887, to B. C. Kirk, T. T. Taber and W. A. Miller.  
<sup>34</sup> S. Tamari, U. S. P. 1,281,702, Oct. 15, 1918, *Chem. Abs.*, 1919, 13, 177. British P. 107,370, 1917; *J.S.C.I.*, 1918, 37, 188A. W. F. Singer, U. S. P. 1,291,207, Jan. 14, 1919, to W. F. Singer, A. V. Fagerstrom, F. Clasby and J. E. Fairbanks; *Chem. Abs.*, 1919, 13, 836.  
<sup>35</sup> H. A. Noyes, U. S. P. 1,528,503, March 3, 1925, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1925, 19, 1477. W. H. Kobbe, U. S. P. 1,612,869, Jan. 4, 1927; *Chem. Abs.*, 1927, 21, 631.  
<sup>36</sup> W. Eberlein, British P. 227,097, 1924; *J.S.C.I.*, 1925, 44, 850B. German P. 407,088, 1924; *J.S.C.I.*, 1925, 44, 319B.  
<sup>37</sup> F. Hauptmeyer, British P. 307,011, 1929, to F. Krupp A.-G.; *Brit. Chem. Abs. B*, 1930, 617.  
<sup>38</sup> M. W. Samuel, British P. 12,765, 1887; *J.S.C.I.*, 1888, 7, 631.  
<sup>39</sup> Carleton Ellis, U. S. P. 1,699,694, Jan. 22, 1929, and 1,795,364, March 10, 1931, to Ellis-Foster Co.; *Chem. Abs.*, 1929, 23, 1238; 1931, 25, 2531.  
<sup>40</sup> F. A. Adamaki, U. S. P. 1,557,231, Oct. 13, 1925; *Chem. Abs.*, 1926, 20, 98.  
<sup>41</sup> J. G. Loch and C. di Battista, U. S. P. 1,438,840, Dec. 12, 1922.  
<sup>42</sup> W. H. Kobbe, U. S. P. 1,693,714, Dec. 4, 1928, to Fleuron, Inc.; *Chem. Abs.*, 1929, 23, 942. R. F. Bacon and H. S. Davis (*Chem. Met. Eng.*, 1921, 24, 65) mention the use of sulphur-sand mixtures in making acid-proof tanks and joints in sewer lines.  
<sup>43</sup> M. W. Samuel, *loc. cit.*  
<sup>44</sup> E. F. A. Bultemann, German P. 116,981, 1900.  
<sup>45</sup> H. A. Noyes, U. S. P. 1,675,376, July 3, 1928, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1928, 22, 3370. Carleton Ellis, U. S. P. 1,665,186, April 3, 1928; *Chem. Abs.*, 1928, 22, 1832.  
<sup>46</sup> Carleton Ellis, U. S. P. 1,664,600, April 3, 1928; *Chem. Abs.*, 1928, 22, 1832.  
<sup>47</sup> R. Zellmann (U. S. P. 1,922,007, Aug. 8, 1933, to Chem. Fabrik von Heyden A.-G.; *Chem. Abs.*, 1933, 27, 5160. German P. 555,338, 1930; *Chem. Abs.*, 1932, 26, 5183) prepared a substance resembling ivory from a coagel of colloidal sulphur in casein. W. R. Willauer (U. S. P. 1,883,209, Oct. 18, 1932, to Marathon Paper Mills Co.; *Chem. Abs.*, 1933, 27, 819) used an emulsion of sulphur and casein in a water-alcohol mixture to join sulphurized fiber board. See also P. D'yachenko, *Plast. Massui*, 1933, (2), 13; *Chem. Abs.*, 1934, 28, 4544.  
<sup>48</sup> M. Darrin, Canadian P. 277,710, 1928; *Chem. Abs.*, 1928, 22, 2840.  
<sup>49</sup> W. H. Kobbe, U. S. P. 1,693,714, Dec. 4, 1928, to Fleuron, Inc.; *Chem. Abs.*, 1929, 23, 942.  
<sup>50</sup> W. W. Barnes, *loc. cit.*  
<sup>51</sup> J. W. Schwab, U. S. P. 1,533,213, April 14, 1925, to Texas Gulf Sulphur Co.; *J.S.C.I.*, 1925, 44, 800B.  
<sup>52</sup> British P. 265,540, 1926, to Rhenania Verein chem. Fabr. A.-G.; *Chem. Abs.*, 1926, 22, 367.  
<sup>53</sup> F. A. Adamaki, *loc. cit.*  
<sup>54</sup> W. Eberlein, British P. 227,197, 1924; *J.S.C.I.*, 1925, 44, 719B.

The investigations of Duecker<sup>60</sup> have shown that the strength of sulphur-sand cements depends mainly on two factors: the per cent voids in the aggregate, and the proportion of sulphur. The effect of the first factor is clearly illustrated by comparing two mixtures possessing the optimum amount of sulphur; the one with sand containing 32.5 per cent voids is 20 per cent stronger than the one with sand having 34.8 per cent voids. This difference in strength is to be expected in the light of data on concrete. Regardless of the grading of the sand, cements of greatest tensile strength are obtained by mixing 40 per cent of sulphur with 60 per cent of sand, and an increase or decrease in amount of sulphur results in a marked loss of strength. Although this is true, more than 40 per cent sulphur is used commercially in order that the cement flow easily. One material that has

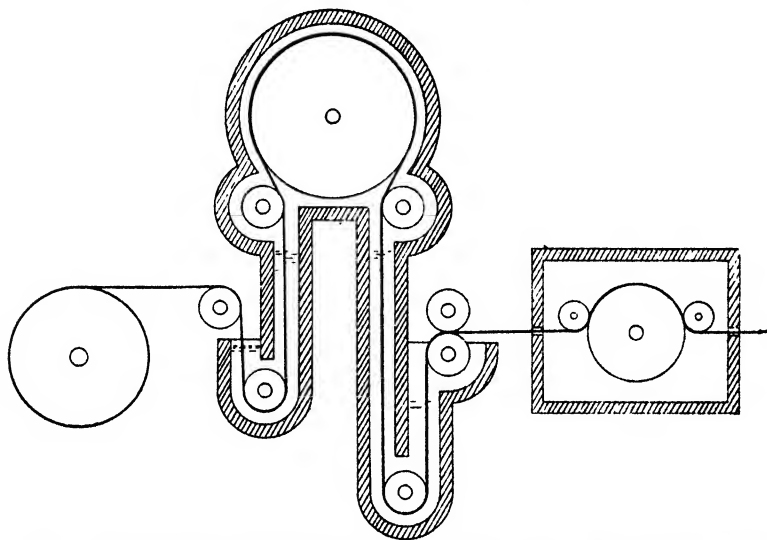


FIG. 158.—Apparatus for Continuously Impregnating or Coating Various Materials. Paper or fabric (from the roll on the left) passes through a sealing fluid into a vacuum chamber, over a heating roll, thence through the impregnating solution and out via squeeze rolls to a drying chamber. The sealing liquid is usually mercury, and the central heating-roll is warmed by an internal circulation of steam under pressure. (O. Minton.)

a marked influence on the workability is carbon black. It retards settling of the aggregate and increases the strength of the cement. The latter property is shown by the fact that a cement containing 70 per cent sulphur has its tensile strength increased from 405 to 670 pounds per sq. in. by replacing 5 per cent of the sand with carbon black.

Sulphur has been used to impregnate articles made of porous material to increase their strength, to make them rigid,<sup>61</sup> to alter their electrical properties,<sup>62</sup> to render them resistant to water and corrosives and, as in the case of wood, to preserve them. The fibrous liners that come in contact with rubber sheets have been impregnated with sulphur to prevent their adhesion to the rubber.<sup>63</sup> The

<sup>60</sup> W. W. Duecker, *Chem. Met. Eng.*, 1924, 11, 583.

<sup>61</sup> W. H. Kobbe, U. S. P. 1,742,145, Dec. 31, 1929, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1930, 24, 1230.

<sup>62</sup> H. B. Todd, U. S. P. 831,902, May 29, 1906. R. C. Lamphier, U. S. P. 850,166, April 16, 1907, to Sangamo Electric Co. H. Hoskins, U. S. P. 1,631,723, June 7, 1927; *Chem. Abs.*, 1927, 21, 3546.

<sup>63</sup> H. A. Endres, U. S. P. 1,808,394, Oct. 19, 1929, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1927, 21, 195. H. J. Conroy and R. A. Hayworth, U. S. P. 1,603,570, Oct. 19, 1926, to Goodyear Tire & Co.; *Chem. Abs.*, 1927, 21, 195.

favorite materials for impregnation may be divided into inorganic (portland cement,<sup>64</sup> plaster of paris,<sup>65</sup> gypsum plaster<sup>66</sup> and diatomaceous earth<sup>67</sup>) and organic (paper,<sup>68</sup> molded paper pulp<sup>69</sup> and wood<sup>70</sup>).

The method in general consists in mere immersion of the article in molten sulphur held at the proper temperature to give the desired impregnation and viscosity.<sup>71</sup> Various materials, such as turpentine,<sup>72</sup> may be added to the sulphur to alter its viscosity and increase impregnation, and pressure and vacuum applied alternately have been suggested to increase the penetration. Ellis,<sup>73</sup> however, sprayed fiber board with an emulsion of sulphur, dried and pressed at about 150°C. Another method, which has been proposed, for incorporating sulphur into fibrous materials is to saturate the material with sodium-polysulphide solution followed by acidifying. This precipitates the sulphur throughout the mass and the process is finished by hot pressing.<sup>74</sup>

The chewing gum named "Chex" consists of sulphur mixed with a vinyl resin as base.<sup>75</sup> A paste of dextrin and selenium (notably the gray form of the element) has been used as a fire-proofing agent in electrical insulation.<sup>76</sup> A mixture of sulphur, selenium, and paper or cloth when pressed in molds and heated gives acid-resisting products.<sup>77</sup>

More extensive discussions of these applications of sulphur and the properties of the resulting materials are given by Kobbe,<sup>78</sup> Wilkinson,<sup>79</sup> Bates<sup>80</sup> and Moll.<sup>81</sup> The use of sulphur for impregnating wood to resist decay and insect attack is described by Bresser<sup>82</sup> and English.<sup>83</sup> A colloidal dispersion of sulphur in a dextrin solution with a  $p_H$  of 7.6 has been recommended as a therapeutic agent for intravenous injection.<sup>84</sup>

<sup>64</sup> S. D. Castle, U. S. P. 343,944, June 15, 1886, to Charles E. Williams and E. W. Dewhurst. A. G. Betts, U. S. P. 918,649, April 20, 1909; *Chem. Abs.*, 1909, 3, 1727. R. F. Bacon, W. H. Kobbe and P. H. Bascom, U. S. P. 1,561,767, Nov. 17, 1925, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1926, 20, 272. W. H. Kobbe, U. S. P. 1,594,417, Aug. 3, 1926, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1926, 20, 3224.

<sup>65</sup> W. H. Kobbe, U. S. P. 1,689,394, Oct. 30, 1928, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1929, 23, 258.

<sup>66</sup> J. W. Emerson, U. S. P. 1,470,260, Oct. 9, 1923; *Chem. Abs.*, 1923, 17, 3913. W. H. Kobbe, U. S. P. 1,693,715 and 1,693,716, Dec. 4, 1928, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1929, 23, 949.

<sup>67</sup> W. H. Kobbe, U. S. P. 1,551,573, Sept. 1, 1925, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1925, 19, 3355.

<sup>68</sup> C. F. Crehore, U. S. P. 74,906, March 3, 1868. G. A. Richter, W. B. Van Arsdel and D. H. White, U. S. P. 1,396,060, Nov. 8, 1921, to Brown Co.; *Chem. Abs.*, 1922, 16, 647. F. A. Burningham, G. A. Richter, W. B. Van Arsdel and D. H. White (U. S. P. 1,396,021, Nov. 8, 1922; *Chem. Abs.*, 1922, 16, 647) for the joint use of sulphur and phenol-aldehyde resins in waterproofing. J. W. Webb, U. S. P. 1,512,729, Oct. 21, 1924; *Chem. Abs.*, 1925, 19, 178. F. H. Coyne, U. S. P. 1,537,752, May 12, 1925; *Chem. Abs.*, 1925, 19, 2132. J. Knaggs (British P. 387,248, 1932, to Portals, Ltd.; *Brit. Chem. Abs. B*, 1933, 302) treated paper, impregnated with casein and rubber latex, with formaldehyde and sulphur to get a waterproof sheet.

<sup>69</sup> J. Gray and C. H. Case, U. S. P. 539,256, Aug. 31, 1897. G. S. Shailor and P. A. Cook, British P. 240,038 and 240,039, 1924; *Chem. Abs.*, 1926, 20, 2233. T. L. Allison and B. Brown, British P. 272,781, Dec. 16, 1926; *Chem. Abs.*, 1928, 22, 1915. W. H. Kobbe, U. S. P. 1,647,528, Nov. 1, 1927; *Chem. Abs.*, 1928, 22, 307. M. M. Frost, U. S. P. 1,726,818, Sept. 3, 1929; *Chem. Abs.*, 1929, 23, 5283. J. Carmie (U. S. P. 1,843,943, Feb. 9, 1932, to Mechanical Rubber Co.; *Chem. Abs.*, 1932, 26, 3057) mixed fiber pulp with rosin size and sulphur, and added alum. Boards made from this material were waterproof.

<sup>70</sup> W. H. Kobbe, U. S. P. 1,599,135, Sept. 7, 1925, to Texas Gulf Sulphur Co.; *Chem. Abs.*, 1926, 20, 3552.

<sup>71</sup> I. L. Roberts (U. S. P. 921,000, May 11, 1909; *Chem. Abs.*, 1909, 3, 2220) has described an apparatus and procedure for impregnating wood with sulphur. O. Minton (U. S. P. 1,322,327, Nov. 18, 1919; *J.S.C.I.*, 1920, 39, 16A) has done the same for rolls of paper or felt. See Fig. 158.

<sup>72</sup> J. W. Emerson, *loc. cit.* See also J. Crespo (U. S. P. 1,401,524, Dec. 27, 1921; *Chem. Abs.*, 1922, 16, 1018) and the work of M. Darrin previously described.

<sup>73</sup> G. H. Ellis, U. S. P. 1,339,690, Jan. 5, 1932, to Insulite Co.; *Brit. Chem. Abs. B*, 1932, 1025.

<sup>74</sup> G. Leuchs and O. Leuchs, German P. 244,818, 1910; *J.S.C.I.*, 1912, 31, 532.

<sup>75</sup> Private communication from G. J. Manson.

<sup>76</sup> E. C. Crocker, U. S. P. 1,891,258, Dec. 12, 1932, to A. D. Little, Inc.; *Brit. Chem. Abs. B*, 1933, 804.

<sup>77</sup> Hungarian P. 101,471, 1930, to Kábelgyár, Ltd.; *Chem. Abs.*, 1931, 25, 2527.

<sup>78</sup> W. H. Kobbe, *Ind. Eng. Chem.*, 1924, 16, 1026; *Eng. News-Rec.*, 1926, 96, 940; *Chem. Abs.*, 1926, 20, 3791.

<sup>79</sup> H. H. Wilkinson, *Chem. Age (N. Y.)*, 1924, 32, 140; *Chem. Abs.*, 1924, 18, 1368. W. N. Wilkinson, *ibid.*, 1923, 31, 67.

<sup>80</sup> P. H. Bates, *Ind. Eng. Chem.*, 1926, 18, 309.

<sup>81</sup> F. Moll, *Korrosion*, 1928, 3, 25; *Chem. Abs.*, 1928, 22, 3508.

<sup>82</sup> A. Bresser, *Korrosion Metallschutz*, 1927, 3, 249; *Chem. Abs.*, 1928, 22, 858.

<sup>83</sup> E. P. English, *J. S. African Inst. Eng.*, 1930, 27, 127; *Chem. Abs.*, 1929, 23, 3787.

<sup>84</sup> J. P. Torligan, U. S. P. 1,960,265, Nov. 13, 1934, to Drug Prod. Co.; *Chem. Abs.*, 1935, 29, 235.



## Chapter 58

# Sulphur-Olefin Resins

The reaction of the halogen addition products of the lower olefin hydrocarbons, especially ethylene dichloride, with sulphides of the alkali and alkaline earth metals has been found to give resinous bodies. Some of these resemble rubber in being elastic and resistant to wear. To an extent they are even superior to rubber since they are not affected by many solvents nor by ozone. However, such plastics have one disadvantage, they contain an impurity with an unpleasant odor, but for some uses this is not necessarily a serious handicap.

### THEORETICAL RESEARCHES

The olefin sulphides attracted considerable attention during the last century and, by 1850, two different forms of ethylene sulphide had been isolated. The first was a white amorphous solid, insoluble in the common solvents, and was obtained by Löwig and Weidmann<sup>1</sup> through the reaction of alcoholic potassium sulphide on ethylene dichloride. Crafts<sup>2</sup> found that this compound distilled at 200°C., yielding a crystalline distillate having a composition corresponding to  $C_2H_4S$ . The latter sulphide was soluble in carbon disulphide, ether, alcohol and benzene. Husemann<sup>3</sup> synthesized the same substance by heating ethylene dibromide with ethylene trithiocarbonate ( $C_2H_4CS_3$ ) at 150°C. Based on vapor density determinations, the double formula,  $(C_2H_4)_2S_2$ , was assigned to the crystalline compound. Corresponding methylene and propylene sulphides were also prepared. In 1886, Masson<sup>4</sup> studied these two forms of ethylene sulphide and showed that both could be isolated by steam distillation from the reaction products of either method of preparation.

Meyer<sup>5</sup> converted the amorphous sulphide into the crystalline by prolonged boiling with phenol. The latter was removed at the end of the reaction by extraction with alkali. A new and permanently amorphous form of ethylene sulphide was also obtained by boiling ethylene dibromide with concentrated aqueous potassium sulphide. In appearance and solubility this product resembled the other amorphous sulphide, but it differed in that it could not be converted into the crystalline dimer by boiling with phenol. It is probable that this material was among the first synthetic plastics, although it was years before the commercial possibilities of such bodies were realized.

Monomeric ethylene sulphide is a liquid (b.p., 55-56°C.) which polymerizes easily. It is prepared by the action of sodium sulphide on chloroethyl thiocyanate and not by the interaction of an olefin halide and an alkali sulphide.<sup>6</sup> The homologous  $\alpha,\beta$ -thiopropane and  $\alpha,\beta$ -thiobutane<sup>7</sup> are reported as being more stable, whereas

<sup>1</sup> Löwig and Weidmann, *Poggendorff's Ann.*, 1830, 46, 81; 1840, 49, 123.

<sup>2</sup> J. M. Crafts, *Ann.*, 1863, 124, 110; 1863, 125, 123; 1863, 126, 320.

<sup>3</sup> Husemann, *Ann.*, 1863, 126, 350.

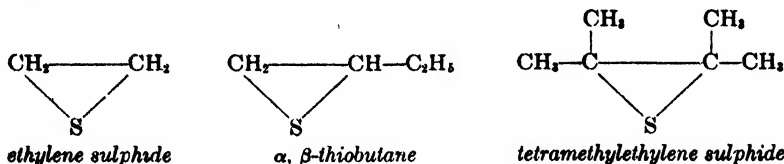
<sup>4</sup> O. Masson, *J.C.S.*, 1886, 49, 233.

<sup>5</sup> V. Meyer, *Ber.*, 1886, 19, 3259; *J.C.S.*, 1887, 52, 228.

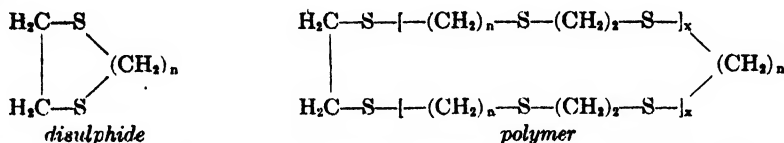
<sup>6</sup> M. Delepine, *Compt. rend.*, 1920, 171, 36; *J.C.S.*, 1920, 118, (1), 526.

<sup>7</sup> M. Delepine and P. Jaffoux, *Compt. rend.*, 1921, 172, 156; *J.C.S.*, 1921, 120 (1), 156.

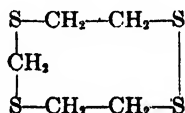
trimethylene sulphide<sup>8</sup> and tetramethylethylene sulphide<sup>9</sup> are polymerized by strong acids. These monomeric compounds have all been formulated as containing ring structures.



Compounds of structure similar to the dimeric ethylene sulphide have been prepared by Tucker and Reid<sup>10</sup> through the action of olefin dihalides on 1,2-ethanedithiol. Both monomeric disulphides and polymeric amorphous materials, were isolated. The following formulas were assigned to the two types of compounds:



Other investigators have also obtained related products. For example, pentamethylene tetrasulphide,



has been isolated by Chakravarti and Saha<sup>11</sup> from the reaction product of 1,2-ethanedithiol on dichloroacetic acid. Thiols of the type,  $\text{HS}-(\text{C}_n\text{H}_{2n}-\text{S})-\text{C}_n\text{H}_{2n}-\text{SH}$ , have been found as by-products in the synthesis of olefin dithiols from olefin halides and alcoholic potassium acid sulphide.<sup>12</sup> Oxidation of p-benzenedithiol with ferric chloride gives an amorphous polymer which, when heated with copper, yields the dimeric compound,  $(\text{C}_6\text{H}_4)_2\text{S}_2$ .<sup>13</sup> Morgan and Burstall<sup>14</sup> have prepared seleno compounds analogous to the olefin sulphides.

As some of the commercial sulphur resins are polysulphides, Thomas and Riding's work on the alkyl polysulphides should be considered. Ethyl bromide reacts with sodium tetrasulphide, yielding a mixture of diethyl disulphide and diethyl pentasulphide. Potassium pentasulphide, on the other hand, gives practically pure diethyl pentasulphide,  $(\text{C}_2\text{H}_5)_2\text{S}_5$ , which is a nonvolatile oil.<sup>15</sup>

#### PREPARATION OF OLEFIN-SULPHIDE RESINS

The olefin-sulphide resins have been studied by Baer and by Patrick and Mnookin.<sup>16</sup> The former prepared tough, rubber-like masses by the action of sulphur and alkali sulphides on olefin halides.<sup>17</sup> These plastics can be molded and

<sup>8</sup> R. W. Bost and M. W. Conn, *Ind. Eng. Chem.*, 1933, 25, 536.

<sup>9</sup> M. A. Youts and P. P. Perkins, *J.A.C.S.*, 1929, 51, 3508.

<sup>10</sup> N. B. Tucker and E. E. Reid, *J.A.C.S.*, 1933, 55, 775.

<sup>11</sup> G. C. Chakravarti and J. M. Saha, *J. Indian Chem. Soc.*, 1928, 5, 453; *Chem. Abs.*, 1929, 23, 97.

<sup>12</sup> J. R. Meadow and E. E. Reid, *J.A.C.S.*, 1934, 56, 2177.

<sup>13</sup> V. C. Parekh and P. C. Guha, *J. Indian Chem. Soc.*, 1934, 11, 95; *Brit. Chem. Abs. A*, 1934, 562.

<sup>14</sup> G. T. Morgan and F. H. Burstall, *J.C.S.*, 1930, 1497; 1931, 173.

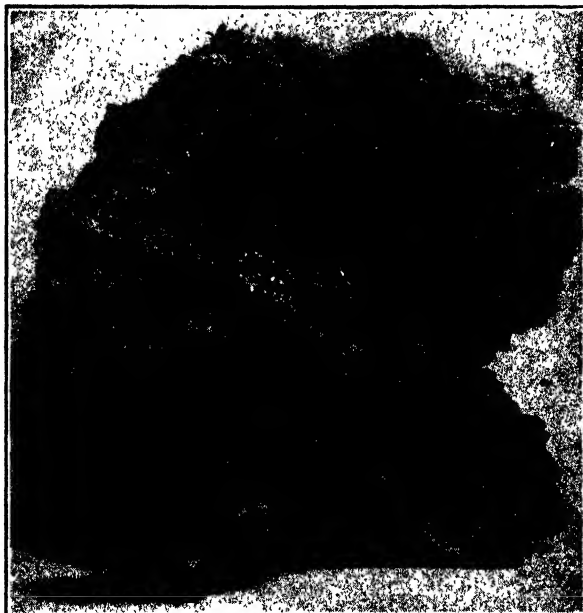
<sup>15</sup> J. S. Thomas and R. W. Riding, *J.C.S.*, 1923, 123, 3371; 1924, 125, 2460.

<sup>16</sup> The work of Patrick and Mnookin is taken up later in the chapter.

<sup>17</sup> J. Baer, *British P.* 279,406, 1926; *Chem. Abs.*, 1928, 22, 2858. Swiss P. 127,540, 132,505, 132,506, 132,507 and 132,508, 1926; *Chem. Abs.*, 1929, 23, 5042. See also French P. 773,073, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1935, 29, 1684.

vulcanized by the same apparatus as is used with natural rubber. Employment of dilute ammonium sulphide as the sulphur-containing reagent resulted in wax-like bodies. Formaldehyde also could be included in the latter reaction, resulting in materials which were reported to be harder than beeswax.<sup>18</sup> According to Baer,<sup>19</sup> the proportion of olefin halide determines the elasticity of the product, whereas he finds that the solubility in carbon disulphide is determined by the sulphur compound used.

Baer did not state whether the resins thus prepared were made through use of the mono- or the polysulphide. In the following cases, the polysulphides are reported to be useful. The rubber-like polymers formed from olefin halides and alkali polysulphides,<sup>20</sup> when heated with an equal weight of raw rapeseed oil, give



Courtesy J. Baer

FIG. 159.—Crude Product from Ethylene Dichloride and Polysulphide.

a factice which is soluble in benzene, chloroform and ethylene chloride.<sup>21</sup> Not only the simple olefin halides, but also such compounds as isoprene dibromide can be used to form these rubber-like substances.<sup>22</sup> Thus, 5 parts of isoprene dibromide were heated with 150 parts of calcium polysulphide solution for 1 hour at 80°C. The product was tough, rich in sulphur and difficultly soluble in many organic solvents. Further, when the condensation product of ethylene chloride and an alkali

<sup>18</sup> J. Baer, U. S. P. 1,913,963, June 6, 1933; *Chem. Abs.*, 1933, 27, 4347. British P. 300,200, 1926; *Brit. Chem. Abs. B*, 1930, 430. Swiss P. 123,325, 1927; *Chem. Abs.*, 1929, 23, 5054. German P. 530,734, 1928; *Chem. Abs.*, 1928, 26, 339.

<sup>19</sup> J. Baer, British P. 302,390, 1927, addn. to 279,400, 1926; *Brit. Chem. Abs. B*, 1929, 236. Australian P. 8901, 1923.

<sup>20</sup> J. Baer, Swiss P. 123,509, 123,510, 123,511, 123,512, 123,513, 123,514 and 123,515, 1926, addns. to 127,540, 1926; *Chem. Abs.*, 1930, 24, 538.

<sup>21</sup> J. Baer, U. S. P. 1,835,537, Oct. 20, 1931; *Chem. Abs.*, 1932, 26, 867. British P. 413,917, 1928; *Chem. Abs.*, 1930, 24, 1249. Swiss P. 142,354, 142,355, 142,356 and 142,357, 1923, addns. to 137,477, 1926 (*Chem. Abs.*, 1930, 24, 4438); *Chem. Abs.*, 1931, 25, 2332.

<sup>22</sup> J. Baer, U. S. P. 1,922,823, Aug. 15, 1932; *Chem. Abs.*, 1933, 27, 5317. British P. 314,334, 1929; *Brit. Chem. Abs. B*, 1931, 173. Swiss P. 142,456, 1929; *Chem. Abs.*, 1931, 25, 2332. German P. 536,121, 1928; *Chem. Abs.*, 1931, 25, 4443.

polysulphide is dissolved in carbon disulphide and the solution emulsified with latex, the resulting pasty mass can be vulcanized in the cold.<sup>28</sup>

Baer has also produced resins by heating tall oil<sup>24</sup> with alkali polysulphides. The products are soluble in carbon disulphide, chloroform and benzene. They can be used as a substitute for colophony, for caulking ships and in rubber compositions.<sup>25</sup>

Olefin-polysulphide resins have also been prepared by Patrick and Mnookin.<sup>26</sup> For example, sodium sulphide (750 g. of  $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) is dissolved in water and the solution boiled with sulphur (300 g.). This produces a solution which contains principally sodium tetrasulphide. The solution is then diluted with water until its specific gravity at 70°C. is approximately that of ethylene dichloride. The latter (500 cc.) is added and the mixture heated under a reflux condenser at 70°C. A yellow rubbery solid separates which can be purified by repeated boiling with water. A solution of calcium tetrasulphide (prepared by saturating with sulphur a slurry of lime at its boiling point) can be reacted in similar manner with the halogen-addition products of the olefins derived from cracked petroleum gases. The resulting material was stated to resemble ethylene polysulphide and could be made tougher and less odorous by the incorporation of an insoluble metallic soap.<sup>27</sup>

These resins resembled soft rubber and could be worked, molded and rolled into sheets at 130–140°C. They were only slightly soluble in organic solvents with the possible exception of carbon disulphide. When halides of olefins higher in the series than ethylene are used the products are less solid and elastic. Employment of metallic sulphides containing smaller proportions of sulphur results in harder bodies. With ethylene chloride, sodium acid sulphide yields a white, brittle, odorless material; polysulphides ranging from  $\text{Na}_2\text{S}_4$  to about  $\text{Na}_2\text{S}_{7.75}$  give what Patrick terms a "hard plastic" whereas a "soft plastic" is formed by compounds with higher sulphur content. The resins harden with age but can be stabilized by heating at about 140°C. for an hour.<sup>28</sup> Patrick<sup>29</sup> suggested that these bodies be mixed with fillers, pigments and accelerators and used in the vulcanization of rubber. A typical mixture was:

Soft ethylene-polysulphide plastic (83% sulphur).....	39.8 parts
Pale crepe rubber.....	39.8
Zinc oxide.....	16.0
Hardwood pitch.....	4.0
Isopropyl-xanthogenate tetrasulphide.....	0.4

Although no sulphur was included in the compositions mentioned above, it can be employed in admixture with equal weights of rubber and olefin polysulphide to produce a body resembling soft vulcanized rubber. The latter does not show any sulphur bloom even though its content of this element is quite high.<sup>30</sup>

<sup>28</sup> J. Baer, U. S. P. 1,899,784, Aug. 2, 1932; *Chem. Abs.*, 1932, 26, 5453. British P. 345,175, 1929; *Chem. Abs.*, 1933, 27, 442. French P. 697,641, 1930; *Chem. Abs.*, 1931, 25, 3199. German P. 593,017, 1934; *Chem. Abs.*, 1934, 28, 3272.

<sup>29</sup> For a description of tall oil see Chapter 36.

<sup>30</sup> J. Baer, U. S. P. 1,907,380, May 2, 1933; *Chem. Abs.*, 1933, 27, 3639. British P. 345,894, 1929; *Chem. Abs.*, 1932, 26, 611. French P. 698,961, 1930; *Chem. Abs.*, 1931, 25, 3503. German P. 541,503, 1929; *Chem. Abs.*, 1932, 26, 2610.

<sup>31</sup> J. C. Patrick, U. S. P. 1,890,191, Dec. 6, 1932; *Chem. Abs.*, 1932, 27, 1724. J. C. Patrick and N. M. Mnookin, British P. 302,370, 1927; *Chem. Abs.*, 1929, 23, 4307. French P. 656,114, 1928; *Chem. Abs.*, 1929, 23, 4030.

<sup>32</sup> J. C. Patrick, U. S. P. 1,906,488, Apr. 2, 1933.

<sup>33</sup> N. M. Mnookin, U. S. P. 1,854,480, April 19, 1932, one-half to J. C. Patrick; *Chem. Abs.*, 1932, 26, 3312. N. M. Mnookin, British P. 330,456, 1930; *Brit. Chem. Abs. B.*, 1931, 769. German P. 533,277, 1929; *Chem. Abs.*, 1934, 28, 271.

<sup>34</sup> J. C. Patrick, U. S. P. 1,854,423, April 19, 1932, one-half to N. M. Mnookin; *Chem. Abs.*, 1932, 26, 3464. J. C. Patrick, British P. 350,673, 1930; *Chem. Abs.*, 1932, 27, 450. French P. 691,743, 1930; *Chem. Abs.*, 1931, 25, 1412.

<sup>35</sup> J. C. Patrick and N. M. Mnookin, U. S. P. 1,890,231, Dec. 6, 1932; *Chem. Abs.*, 1932, 27, 1784. British P. 320,549, 1930; *Chem. Abs.*, 1932, 27, 443. J. C. Patrick, Canadian P. 339,563, 1932; *Chem. Abs.*, 1932, 27, 2661.

Another product of a similar nature was prepared by producing the polymer in the presence of a dispersing agent. The procedure gave a latex which could be coagulated in the presence of the constituents of the final compounded rubber, or it could be used to impregnate fabrics. The dispersing agent recommended was precipitated magnesium hydroxide, but others such as gelatin, glue and peptized starch were mentioned as possibilities.<sup>21</sup> Thus, 50 cc. of a sodium hydroxide solution containing 290 g. of sodium hydroxide per l. and 100 cc. of a solution of magnesium chloride containing 172 g. per l. were added to 1000 cc. of calcium polysulphide solution. The latter contained a polysulphide of the empirical formula  $\text{CaS}_{4.7}$  and had a specific gravity of 1.272. A semi-gelatinous dispersion of magnesium hydroxide resulted. Then 157 cc. of ethylene dichloride were added in small portions, keeping the temperature down to 66-80°C. until all of the halide



Courtesy J. Baer

FIG. 160.—Product Shown in Fig. 159 After Rolling.

was added. At the end of the reaction the temperature was raised to 80-88°C. until the odor of the halide had disappeared. The olefin-polysulphide plastic formed in this reaction mixture was a latex-like dispersion which settled to the bottom of the container. The supernatant liquid was decanted and the latex washed by decantation until soluble salts were removed.

Olefin-polysulphide resins are improved by hot curing. Patrick<sup>22</sup> has reported that the hot cure can be controlled by adding chlorinated rubber (15 per cent chlorine), chloroprene or metallic halides so that the final product is more resistant to solvent action. It has been found by Ellis<sup>23</sup> that the olefin sulphide resins are greatly improved by forming them in the presence of the substances produced by the action of sulphur monochloride on phenols. The elasticity was considerably increased and the mixed resin was less liable to crumble during milling.

<sup>21</sup> J. C. Patrick, U. S. P. 1,950,744, Mar. 13, 1934; *Chem. Abs.*, 1934, 23, 2541. U. S. Reissue 19,307, June 13, 1934; *Chem. Abs.*, 1934, 23, 4843. British P. 230,000, 1929, and 349,067, 1930; *Chem. Abs.*, 1932, 26, 4981; *Chem. Abs.*, 1933, 27, 2300. Canadian P. 230,001, 1932; *Chem. Abs.*, 1933, 26, 2621. French P. 709,155, 1930, and 719,312, 1931; *Chem. Abs.*, 1932, 26, 237, 2344. German P. 579,632, 1933; *Chem. Abs.*, 1934, 23, 1154. See also German P. 601,920, 1934; *Chem. Abs.*, 1934, 23, 7444.

<sup>22</sup> J. C. Patrick, U. S. P. 1,952,490, June 13, 1934; *Chem. Abs.*, 1934, 23, 4543. U. S. Reissue 19,437, Mar. 5, 1935; *Chem. Abs.*, 1935, 29, 3039.

<sup>23</sup> Carlston Ellis, U. S. P. 1,927,939, Sept. 24, 1932, to Ellis-Foster Co.; *Chem. Abs.*, 1932, 27, 5007.

Previous to reaction with an olefin halide, the alkali sulphide solution may be stabilized by refluxing for 15-20 hours. Further modifications include the employment of a water-miscible alcohol and freshly slaked lime. The former increases the solubility of the halide whereas the latter hardens the product. Thus, a hard thermoplastic material is formed by adding 40 g. of freshly slaked lime (in 200 cc. of water) to 177 g. of sodium polysulphide ( $\text{Na}_2\text{S}_{2.2}$ ) in 1 l. of water. The mixture is thoroughly agitated, about 180 cc. of ethyl alcohol are added, followed by 180 cc. of ethylene dichloride at such a rate that the temperature does not rise above 63°C. The product is greenish blue and coarsely granular. It is washed with water and then with 0.5 *N* acid to remove inorganic salts. In washing, the material also loses its color. After drying to constant weight, it can be mixed with fillers and molded at 132-163°C.<sup>24</sup> If one part of "hard plastic" is heated with up to 10 parts of sulphur at 127-132°C. for 3-4 days, a tough, strong, rubber-like material is produced. The color is greenish yellow and no tendency to become crystalline is exhibited.<sup>25</sup>

#### PROPERTIES AND USES OF THE OLEFIN-POLYSULPHIDE RESINS

The olefin-polysulphide resins resemble rubber fairly closely in physical properties and therefore have been suggested as substitutes for it.<sup>26</sup> It should be noted that such products are oil-resistant and this is the main incentive which has led to their study and use.<sup>27</sup> A typical formula for compounding Thiokol A is the following:

Thiokol A . . . . .	100 parts
Diphenylguanidine . . . . .	0.25
Tetramethylthiuram disulphide . . . . .	0.10
Rubber . . . . .	5.
Zinc oxide . . . . .	10.
Carbon black . . . . .	25.
Stearic acid . . . . .	0.50

In this composition, the diphenylguanidine acts as a softener in the earlier part of the mixing, enabling the rest of the ingredients to be added without getting the material overheated. The latter condition is to be avoided as otherwise the odor will be unduly strong. As the other ingredients, especially the stearic acid, carbon black and zinc oxide, are added the mass becomes stiffer. To avoid too great a stiffening, the tetramethylthiuram disulphide is added. It does not act fast enough on Thiokol A to be used as an initial softener, but it differs from diphenylguanidine in that the presence of acids and carbon black does not interfere with its plasticizing action. The rubber is added to decrease the cold flow, to in-

<sup>24</sup> J. C. Patrick, U. S. P. 1,923,392, Aug. 22, 1933, and 1,990,202, Feb. 5, 1935; *Chem. Abs.*, 1933, 27, 5190; 1935, 29, 1903. British P. 354,310, 354,394, 360,890, 1930; *Brit. Chem. Abs.* B, 1931, 936; 1932, 236. Canadian P. 320,090 and 320,092, 1932; *Chem. Abs.*, 1932, 26, 2621. German P. 554,112 and 554,897, 1930; *Chem. Abs.*, 1932, 26, 5183, 6080.

<sup>25</sup> J. C. Patrick, U. S. P. 1,990,203, Feb. 5, 1935; *Chem. Abs.*, 1935, 29, 1903.

<sup>26</sup> N. Zelinskii, Y. Denisenko, M. Eventova and S. Khromov, *J. Rubber Ind. (U. S. S. R.)*, 1930, 10, 45; *Chem. Abs.*, 1933, 27, 6016. R. Pummerer, *Angew. Chem.*, 1934, 47, 209; *Chem. Abs.*, 1934, 28, 4267. The olefin polysulphides are made under the two trade names "Ethanite" (Wilfred Smith, Ltd., London) and "Thiokol A." A booklet published by the Thiokol Corp., Yardville, N. J., and dated June, 1934, applies the name "Thiokol A" to the olefin polysulphides previously known simply as "Thiokol." For use of "Thiorubber" in manufacturing see: E. Chernikov and A. Osterov, *J. Rubber Ind. (U. S. S. R.)*, 1934, 11, 228; *Chem. Abs.*, 1935, 29, 2359. For other reviews see L. Borodulin, *J. Rubber Ind. (U. S. S. R.)*, 1934, 11, 198; *Chem. Abs.*, 1935, 29, 2779. M. Tartakovskii, *Kozhev.-Obuv. Prom. U. S. S. R.*, 1933, 12, 624; *Chem. Abs.*, 1935, 29, 2779.

<sup>27</sup> W. J. S. Naunton, M. Jones and W. F. Smith, *Trans. Inst. Rubber Ind.*, 1933, 9, 169; *Chem. Abs.*, 1934, 28, 2599. *British Plastics*, 1933, 4, 440; 1935, 6, 396. *J.S.C.I.*, 1932, 51, 694; 1935, 54, 917. A. H. Smith, *Kautschuk*, 1933, 9, 186; *Chem. Abs.*, 1934, 28, 5713. Cf. J. Baer, *ibid.*, 1934, 10, 55 and reply by A. H. Smith, *ibid.*, 1934, 10, 55; *Chem. Abs.*, 1934, 28, 4628, as to priority in the manufacture of these oil-resistant substances.

crease the flexibility at low temperatures and to improve the molding properties. The zinc oxide assists in the heat cure of the product after fashioning, whereas the carbon black increases the strength and further decreases the cold flow. Finally, the stearic acid is added as a mold lubricant.

Such a mixture requires a cure of about 50 minutes at 142°C. to raise the tensile strength and to decrease the cold flow. It will then resist the swelling action of most liquids encountered in industry. Thus, gasoline, motor oil, fuel oil, carbon tetrachloride, Duco Thinner and turpentine cause no dimensional increase after two years' immersion. Dilute acids do not harm Thiokol A. Even strong



Courtesy Thiokol Corporation

FIG. 161.—Mixing Thiokol in Vats.

acetic acid causes no degradation, but oxidizing acids (nitric and chromic) attack the olefin polysulphides.<sup>38</sup> Caustic alkali, but not sodium carbonate, hardens Thiokol A so that it will break on bending. Oxygen and ozone do not attack Thiokol A; samples which were exposed to the weather showed no signs of cracking. Kartzev and Verbo<sup>39</sup> stated that up to 5 per cent Thiokol in rubber mixtures used in automobile tires increased the tensile strength and resistance to wear of the vulcanizates.

The principal disadvantage of the olefin polysulphides is their marked odor.<sup>40</sup> However, as has been previously noted, this has not prevented their being employed for some purposes. Thus, asbestos impregnated with Thiokol A has been used to seal the joint around the edge of the floating roofs of oil tanks.<sup>41</sup> The seal has shown its ability to stand up against sunlight, weathering and sour crude

<sup>38</sup> *Chem. Met. Eng.*, 1932, 39, 318, 654.

<sup>39</sup> V. N. Kartzev and P. P. Verbo, *J. Rubber Ind. (U. S. S. R.)*, 1934, 11, 202; *Chem. Abs.*, 1935, 29, 2390.

<sup>40</sup> The odor is due principally to ethylene mercaptan. N. D. Zelinsky, Ya. I. Denisenko, M. S. Eventova and S. I. Khromov, *J. Rubber Ind. (U. S. S. R.)*, 1934, 11, 111; *Chem. Abs.*, 1934, 28, 7590.

<sup>41</sup> J. P. Bushnell, *Rubber Age (N. Y.)*, 1933, 33, 107; *Chem. Abs.*, 1933, 27, 4137

oils. A number of applications employ Thiokol A as a protective coating for natural rubber. The latter furnishes the required elasticity, partially neutralizing the cold flow of the polysulphide. In this way gaskets<sup>42</sup> for oil lines, rubber hose for handling petroleum distillates,<sup>43</sup> and printers' rollers and blankets<sup>44</sup> have been made. Again, the olefin polysulphides have been used in the manufacture of insulated cables.<sup>45</sup> Although Thiokol A can be bonded to metal, it is not especially recommended for this. However, Thompson<sup>46</sup> has succeeded in attaching it and other rubber-like materials to rigid surfaces by an intermediate layer of a phenol-formaldehyde condensation product. The latter and other types of synthetic resins have been formed in admixture with olefin polysulphides by dissolving the sulphide in one component of the resin and then adding the other.<sup>47</sup>

#### RESINS RELATED TO THE OLEFIN SULPHIDES

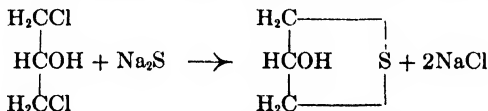
Resins made from the dichlorohydrins of glycerol form a group closely related to the olefin sulphides.  $\beta$ -Dichlorohydrin (2,3-dichloro-1-propanol) is the chloride of allyl alcohol; therefore the sulphides formed from it might be regarded as olefin derivatives. However, the  $\alpha$ -compound (1,3-dichloro-2-propanol) cannot be considered a derivative of an unsaturated alcohol. Nevertheless, both  $\alpha$ - and  $\beta$ -dichlorohydrin are discussed here since they exhibit some similarities.

In 1873, Claus<sup>48</sup> reported that a review of the earlier work of Carius<sup>49</sup> on the formation of glycerol dichlorohydrin had confirmed the formation of sulphur-containing by-products. The method which these investigators used involved the reaction of sulphur monochloride on glycerol.



A 62 per cent yield of purified product was obtained by Claus. This product possibly contained some  $\beta$ -dichlorohydrin although it consisted principally of the  $\alpha$ -compound. The latter has also been prepared in 70 per cent yields by passing gaseous hydrogen chloride into glycerol containing a small amount of acetic acid.<sup>50</sup>

Carius<sup>51</sup> prepared thioglycerols by the action of potassium hydrogen sulphide on the above-mentioned chlorohydrins. The thioglycerols were viscous substances with disagreeable odors. They dissolved in alcohol and lost hydrogen sulphide on heating. Lilienfeld<sup>52</sup> has studied these compounds and especially those formed



<sup>42</sup> W. B. Damsel and W. C. Damsel, U. S. P. 1,931,922, Oct. 24, 1933; *Chem. Abs.*, 1934, 28, 593

<sup>43</sup> J. P. Bushnell, *Rubber Age* (N. Y.), 1933, 34, 15

<sup>44</sup> W. H. Stevens, *India-Rubber J.*, 1933, 86, 591; *Brit. Chem. Abs. B*, 1933, 1018. R. R. Lewis and A. J. Weiss, U. S. P. 1,846,810, Feb. 23, 1932, to Vulcan Proofing Co.; *Chem. Abs.*, 1932, 26, 2562. British P. 387,811, Feb. 16, 1933; *Chem. Abs.*, 1933, 27, 5910. See also U. S. P. 1,971,044, Aug. 21, 1934, *Chem. Abs.*, 1934, 28, 6260. J. P. Bushnell, *Rubber Age* (N. Y.), 1933, 34, 118.

<sup>45</sup> J. C. Patrick, British P. 370,741, 1932; *Chem. Abs.*, 1935, 27, 3543. W. C. Hayman, British P. 385,422, 1932, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 4441. See also *Chem. Ind.*, 1934, 34, 444. For a report on the diffusion of water through various insulating materials, including Thiokol A, see D. B. Hermann, *Rubber Age* (N. Y.), 1934, 36, 73; *Chem. Abs.*, 1935, 29, 1174.

<sup>46</sup> O. A. Thompson, U. S. P. 1,931,309, Oct. 17, 1933, to B. F. Goodrich Co.; *Chem. Abs.*, 1934, 28, 374. British P. 388,776, 1933; *Chem. Abs.*, 1933, 27, 5909.

<sup>47</sup> D. F. Twiss and A. E. T. Neale, British P. 420,386, 1933, to Dunlop Rubber Co., Ltd.; *Brit. Chem. Abs. E*, 1935, 711; See also French P. 774,370, 1934, to Soc. anon. des pneumatiques Dunlop. *Chem. Abs.*, 1935, 29, 2261.

<sup>48</sup> A. Claus, *Ann.*, 1873, 168, 42; *J.C.S.*, 1873, 26, 1120.

<sup>49</sup> L. Carius, *Ann.*, 1862, 122, 73; 1862, 124, 221.

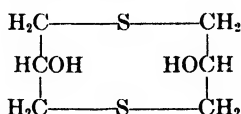
<sup>50</sup> German P. 197,308 and 197,309, 1906, to C. F. Böhringer & Söhne, *J.S.C.I.*, 1908, 27, 713. See also J. B. Conant and O. R. Quayle, "Organic Syntheses," John Wiley & Sons, Inc., New York, 1922, II, 29.

<sup>51</sup> L. Carius, *loc. cit.*

<sup>52</sup> L. Lilienfeld, U. S. P. 1,018,329, Feb. 20, 1912; *J.S.C.I.*, 1912, 31, 302. British P. 26,928, 1910, and 25,246, 1911; *J.S.C.I.*, 1912, 31, 122, 786. French P. 426,988, 1911; *J.S.C.I.*, 1912, 31, 329.



by the action of inorganic sulphides on glycerol dichlorohydrin. He believed the reaction to be as indicated in the preceding equation. The cyclic sulphide polymerized with the formation of a disulphide,

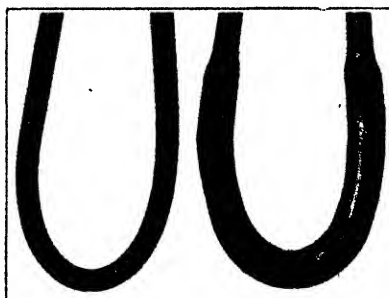


The  $\beta$ -dichlorohydrin of glycerol gave analogous products. The original material obtained from the reaction was a viscous fluid. Heat transformed this liquid into a solid, pliable, elastic mass, a conversion which could be carried out *in situ* after impregnating fabric with the thioglycerol. Prolonged heating resulted in a horny body. Lilienfeld intended to use these products as substitutes for rubber or horn and in the manufacture of threads and adhesives.

In his earlier work Lilienfeld used at least stoichiometric amounts of alkali sulphides. Later, resins formed by employing less than the equivalent amount of sulphide (or the corresponding selenium or tellurium compound) were reported as being possible reagents in organic synthesis, and he contemplated using them for medical purposes.<sup>53</sup> Molded articles were made by incorporating urea-aldehyde resins into the thioglycerol compound.<sup>54</sup>

FIG. 162

Comparison of Thiokol and Rubber. On the left is a Thiokol-sheathed electrical cord (Oilproof Okocord) and on the right a rubber-sheathed cord. Both were immersed in gasoline for 30 days.



Courtesy Okonite Company

A rayon thread which resembled wool was produced by spinning rayon into a dispersion of kieselguhr or clay. To the coagulating bath there was added 1,2-epithio-3-hydroxypropane (3-hydroxy-1,2-propylene sulphide) which acted as an adhesive.<sup>55</sup> Blumfeldt<sup>56</sup> obtained a liquid condensation product, which was insoluble in water but soluble in alcohol, by treating epichlorohydrin (3-chloro-1,2-epoxypropane) with a solution of sodium sulphide.

Egloff<sup>57</sup> combined sulphur directly with the pressure distillate produced by cracking Californian petroleum. Five to 10 parts of sulphur were added to 90-95 parts by weight of the oil and the mixture was refluxed at about 250°C. under a pressure of 50 pounds per square inch. The oil reacted with the sulphur and the lighter vapors escaped through the throttled outlet of the still. The reaction was completed in 6 hours or more, depending on the oil. A resinous pitch and

<sup>53</sup> L. Lilienfeld, British P. 335,980, 1933; *Chem. Abs.*, 1933, 27, 4246. French P. 758,359, 1934; *Chem. Abs.*, 1934, 28, 3079.

<sup>54</sup> L. Lilienfeld, British P. 363,772, 1930; *Chem. Abs.*, 1933, 27, 2320. Austrian P. 133,507; *Chem. Abs.*, 1933, 27, 4112.

<sup>55</sup> British P. 384,440, 1931, to Deutsche Bekleidungsind. G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 103.

<sup>56</sup> A. E. Blumfeldt, Swiss P. 137,478, 1928; *Chem. Abs.*, 1930, 24, 4426.

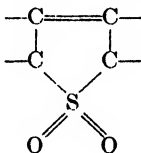
<sup>57</sup> G. Egloff, U. S. P. 1,896,227, Feb. 7, 1933, to Universal Oil Products Co.; *Chem. Abs.*, 1933, 27, 2571.

some oil, which could be decanted, were formed. Sulphuryl chloride brought about a similar resinification.

Amino and hydroxy compounds are formed when polychlorinated paraffins are heated with solutions of ammonia or caustic alkali, respectively. If the products still contain chlorine or if they are unsaturated, they will react with sulphur or metallic sulphides to form oils. For example heating hexachlorinated hard paraffin with alcoholic ammonia furnished nitrogenous bodies. Forty parts of this material were mixed with 200 parts of a saturated solution of hydrogen sulphide in 10 per cent alcoholic potassium hydroxide. The mixture was heated at 130-140°C. for 3 hours. The nitrogen-containing product possessed an average of one thiol group per molecule. It was free from chlorine and was more unsaturated than previous to sulphurization.<sup>55</sup> Oxidation of the sulphidic bodies thus obtained yielded sulphonic acids which were said to be applicable in the textile and pharmaceutical industries.<sup>56</sup>

#### OTHER OLEFIN-SULPHUR RESINS

Sulphur dioxide adds to olefin hydrocarbons to form sulphones. The formulas that have been assigned by De Bruin and Staudinger<sup>57</sup> in the case of butadiene hydrocarbons are cyclic sulphones of the general type,



Staudinger obtained these monomeric products by using such anticatalysts as pyrogallol and hydroquinone in order to prevent polymerization. Eigenberger<sup>58</sup> reported that he had obtained two isoprene sulphones of which the less soluble may have been a polymer.

When the simple olefins are placed in a sealed tube with liquid sulphur dioxide, the oxide adds to the double bond, and a white, glassy solid results. The reaction does not take place in the dark, but is complete in a few days if the tube is exposed to sunlight. The products are soluble in chloroform and acetylene tetrachloride. Matthews and Elder<sup>59</sup> stated that these resins may be employed as substitutes for celluloid or may be mixed with the latter material to reduce its inflammability. The heteropolymers of cyclohexene and cyclohexadiene with sulphur dioxide have been prepared by Seyer and King.<sup>60</sup> The reaction with cyclohexene, but not with cyclohexadiene, occurred only in the presence of oxygen. Frederick, Cogan and Marvel<sup>61</sup> studied the condensation product of cyclohexene and sulphur dioxide. They demonstrated that it was a long chain of cyclohexylene radicals separated by sulphone groups. Acetylation showed that there was a hydroxyl group at the end of the chain. From the analysis of the chloroacetate and the cryoscopic determination of the molecular weights of the acetyl and

<sup>55</sup> K. Keller, U. S. P. 1,950,850, Mar. 13, 1934, to General Aniline Works, Inc.; *Chem. Abs.*, 1934, 28, 3420. British P. 360,993 and 361,856, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1890.

<sup>56</sup> British P. 361,357, 1930, addn. to 360,993, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1890. French P. 704,691, 1930; *Chem. Abs.*, 1931, 25, 4555.

<sup>57</sup> G. de Bruin, *Verslag Akad. Wetenschappen*, 1914, 23, 445; *Chem. Abs.*, 1915, 9, 623. H. Staudinger, French P. 698,357, 1930; *Chem. Abs.*, 1931, 25, 3360. German P. 506,839, 1929; *Chem. Abs.*, 1931, 25, 522. E. Sauter, (*Z. Krist.*, 1932, 83, 840; *Chem. Abs.*, 1933, 27, 2362) has studied the x-ray diffraction diagrams of the monomeric sulphones.

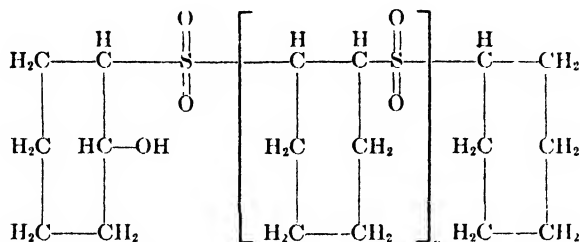
<sup>58</sup> E. Eigenberger, *J. prakt. Chem.*, 1930, 127, 307; 1931, 129, 312; *Chem. Abs.*, 1931, 25, 276, 2969.

<sup>59</sup> F. E. Matthews and H. M. Elder, British P. 11,635, 1914; *J.S.C.I.*, 1915, 34, 670.

<sup>60</sup> W. F. Seyer and E. G. King, *J.A.C.S.*, 1933, 55, 3140.

<sup>61</sup> D. S. Frederick, H. D. Cogan and C. S. Marvel, *J.A.C.S.*, 1934, 56, 1815.

chloroacetyl derivatives in dioxane, the molecular weight was considered to be approximately 6000. That would correspond to a value of about 39 for "n" in the formula,



The reaction between sulphur monochloride and olefins<sup>65</sup> is strongly exothermic and often yields resinous materials. The addition of sulphur monochloride to 2,3-dimethylbutadiene, both in carbon disulphide, gave an oil after evaporation of the solvent *in vacuo*.<sup>66</sup> Distillation of this oil yielded a solid polymer or decomposition product. Below 100°C., bis(2-chloropropyl) sulphide can be obtained from propylene<sup>67</sup> and a similar compound has been prepared from commercial amylene. The formula, (C<sub>4</sub>H<sub>9</sub>ClS)<sub>n</sub>, was assigned to the latter substance since, on reduction, it formed diamyl disulphide, C<sub>8</sub>H<sub>18</sub>-S-S-C<sub>8</sub>H<sub>18</sub>.<sup>68</sup> Above 100°C., both butylene and propylene are converted into black resins by sulphur chloride. 1-Bromo-2,2'-dichlorodiethyl sulphide,<sup>69</sup> bis(3-iodopropyl) sulphide<sup>70</sup> and bis(chloroacetyl) sulphide<sup>71</sup> all decompose on standing. In an attempt to compare the electronegativities of the two propyl radicals, von Braun and Murjahn<sup>72</sup> treated n-propyl-isopropyl sulphide with cyanogen bromide. Instead of the desired splitting into bromide and thiocyanate, the mass resinified.

Twiss and Neale<sup>73</sup> refluxed ethylene dichloride with a solution of sodium thiosulphate in aqueous alcohol. The product was acidified with acetic acid and heated with hydrogen peroxide, furnishing a rubber-like material. The latter was reported to increase the oil-resistance of rubber compositions.

#### ALDEHYDE-SULPHUR RESINS

The thioaldehydes are simply related to the normal aldehydes. In the thio compound, the oxygen atom of the aldehyde group is replaced by a sulphur atom, giving substances of the general formula, RCHS. A polymer of the simplest member of the series, thioformaldehyde, was described by Fromm and Soffner.<sup>74</sup> This compound (m.p., 216°C.) was furnished by the reaction of hydrogen sulphide

<sup>65</sup> This reaction may be applied to the determination of olefin hydrocarbons. W. F. Faragher, J. C. Morrell and I. M. Levine, *Ind. Eng. Chem., Anal. Ed.*, 1930, 2, 18.

<sup>66</sup> A. D. Macallum and G. S. Whitby, *Trans. Roy. Soc. Can.*, 1928, 22, 33, *Chem. Abs.*, 1928, 22, 2079.

<sup>67</sup> W. J. Pope and J. L. B. Smith, *J.C.S.*, 1921, 119, 397. See also S. Coffey, *J.C.S.*, 1921, 119, 94. Difficulty has been encountered in preparing the isomeric bis(3-chloropropyl) sulphide by replacement of hydroxyl groups in bis(3-hydroxypropyl) sulphide. Noncrystalline masses were formed by phosphorus trichloride and the other usual reagents. G. M. Bennett and A. L. Hock, *J.C.S.*, 1925, 127, 2673.

<sup>68</sup> Guthrie, *Ann.*, 1860, 113, 270; 1862, 121, 115; F. Beilstein, "Handbuch der organischen Chemie," 3rd Ed., L. Voss, Hamburg, 1893, I, 118, 365.

<sup>69</sup> W. E. Lawson and T. P. Dawson, *J.A.C.S.*, 1927, 49, 3119.

<sup>70</sup> E. V. Bell, G. M. Bennett and A. L. Hock, *J.C.S.*, 1927, 1803. Cf. E. Wedekind, *Ber.*, 1925, 58, 2510; *Brit. Chem. Abs. A.*, 1926, 146.

<sup>71</sup> F. Arndt and N. Bekir, *Ber.*, 1930, 63, 2390; *Chem. Abs.*, 1931, 25, 914.

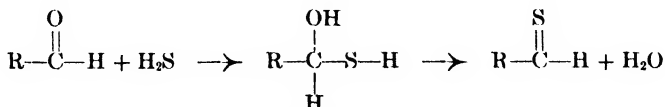
<sup>72</sup> J. v. Braun and R. Murjahn, *Ber.*, 1926, 59, 1202; *Brit. Chem. Abs. A.*, 1926, 829.

<sup>73</sup> D. F. Twiss and A. E. T. Neale, *British P.* 412,849, 1934, to Dunlop Rubber Co. Ltd.; *Chem. Abs.*, 1934, 28, 7595. See also French P. 768,979, 1934, to Soc. anon. des pneumatiques Dunlop; *Chem. Abs.*, 1935, 29, 522.

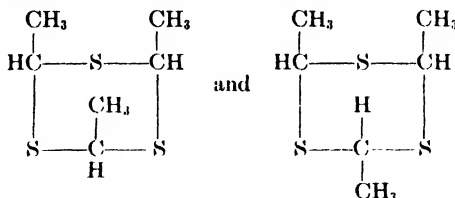
<sup>74</sup> E. Fromm and M. Soffner, *Ber.*, 1924, 57, 371; *Chem. Abs.*, 1924, 18, 1983. Thioformaldehyde has been observed to condense with phenol to form a resinous body. G. Brunn, *Austrian P.* 100,564, 1921; *Brit. Chem. Abs. B.*, 1926, 890.

with formaldehyde and was probably a dithiol,  $\text{HS}-\text{CH}_2-\text{S}-(\text{CH}_2-\text{S})_x-\text{CH}_2\text{SH}$ . On treatment with hydrogen chloride, it gave another material which melted at  $247^\circ\text{C}$ . and which was believed to be polythioformaldehyde,  $(\text{CH}_2\text{S})_n$ . The molecular weight of neither of the compounds was determined. Fromm and Soffner believed, however, that it was doubtful that the number of carbon atoms was equal to three.<sup>75</sup>

Borgeson and Wilkinson<sup>76</sup> made a study of the reactions which take place when aldehydes are dissolved in liquid hydrogen sulphide. Benzaldehyde,<sup>77</sup> p-tolualdehyde and cinnamaldehyde all yielded gelatinous products, the general reaction being



A crystalline substance, on the other hand, was isolated in the case of furfural.<sup>78</sup> Further, it has been found that acetaldehyde with hydrogen sulphide in the presence of dilute hydrochloric acid forms monothioparaldehyde. This is converted into  $\alpha$ -trithioacetaldehyde by 2N hydrochloric acid.<sup>79</sup> There are two trithioacetaldehydes, both of which are crystalline compounds. They are represented by the following cis and trans formulas:<sup>80</sup>



The thioaldehydes polymerize rather easily with the formation of resins. In fact, the monomeric thioaldehydes are relatively rare.<sup>81</sup> Renard<sup>82</sup> prepared dithio-trioxymethylene as a hard, wax-like solid melting at  $80-82^\circ\text{C}$ . Delepine,<sup>83</sup> in 1888, observed the formation of a resinous substance in the reaction of ammonium sulphide with formaldehyde. This material was assigned the formula,  $(\text{CH}_2)_5\text{S}_2\text{N}_2$ , and the name pentamethylenediaminedisulphine. It is resistant to alkalies and has been employed in chloroform solution as a coating and impregnant.<sup>84</sup> It can also be used in molding compositions both as a binder and as a plasticizer for other resins.<sup>85</sup> Further, this sulphine and the related selenium compound<sup>86</sup> are stated to be vulcanization accelerators.

<sup>75</sup> Cf. O. Hinsberg, *J. prakt. Chem.*, 1933, 138, 207; *Chem. Abs.*, 1934, 28, 96.

<sup>76</sup> R. W. Borgeson and J. A. Wilkinson, *J.A.C.S.*, 1929, 51, 1453.

<sup>77</sup> Polymeric selenobenzaldehydes have been obtained from the action of hydrogen selenide on benzaldehyde. L. Vanino and A. Schinner, *J. prakt. Chem.*, 1915, 91, 116; *Chem. Abs.*, 1915, 9, 1609. L. Szperl and V. Viorogorsky, *Roczniki Chem.*, 1932, 12, 270; *Chem. Abs.*, 1933, 27, 278.

<sup>78</sup> R. E. Meints and J. A. Wilkinson, *J.A.C.S.*, 1929, 51, 803. See also G. M. Quam, *J.A.C.S.*, 1925, 47, 103.

<sup>79</sup> E. Müller and G. Schiller, *J. prakt. Chem.*, 1927, 116, 175; *Chem. Abs.*, 1927, 21, 2872.

<sup>80</sup> E. Fromm and L. Engler, *Ber.*, 1925, 58, 1916; *Chem. Abs.*, 1926, 20, 578. E. V. Bell, G. M. Bennett and F. G. Mann, *J.C.S.*, 1929, 1462. See also S. V. Lebedev and M. Platonov, *Ber.*, 1926, 59, 762; *Chem. Abs.*, 1926, 20, 2657.

<sup>81</sup> A. Schönberg (*Ber.*, 1929, 62, 195; *Chem. Abs.*, 1929, 23, 2708) reports that, in the thioketone series, the same changes in constitution which increase the tendency of free methyls to polymerize also increase the tendency of the thioketones to do the same. Cf. the dimeric oxides and sulphides obtained in the autoxidation of thiobenzophenone, H. Staudinger and H. Freudenberger, *Ber.*, 1928, 61, 1836; *Chem. Abs.*, 1929, 23, 130.

<sup>82</sup> A. Renard, *Ann. chim. phys.*, 1879 (5), 17, 307. *Compt. rend.*, 1876, 82, 562; *J.C.S.*, 1876, 30, 64.

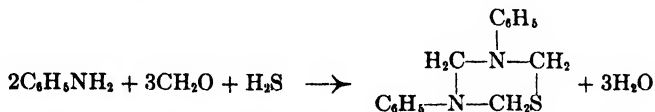
<sup>83</sup> M. Delepine, *Ann. chim. phys.*, 1898 (7), 15, 570; *J.C.S.*, 1899, 76 (1), 410.

<sup>84</sup> German P. 246,038, 1910, to S. Diesser; *J.S.C.I.*, 1912, 31, 595.

<sup>85</sup> M. Landecker, U. S. P. 1,991,398, Feb. 19, 1935, to American Cyanamid Co.; *Chem. Abs.*, 1935, 29, 2263. British P. 358,089, to Thomas & Co., G.m.b.H.; *Chem. Abs.*, 1932, 26, 6184. See also A. Machado, *Rev. chim. pura applicado*, 1928, 3, 129; *Chem. Abs.*, 1931, 25, 5140.

<sup>86</sup> P. Scholtz, German P. 540,631, 1927, to Metallgesellschaft A.-G.; *Chem. Abs.*, 1932, 26, 2348.

Products similar to that produced by Delepine have been studied by Levi.<sup>87</sup> Substituted thialdines were obtained by the reactions of amine sulphides with formaldehyde. For example, aniline<sup>88</sup> condensed with formaldehyde and hydrogen sulphide in the following manner:



The same investigator also isolated substituted ammonium salts of thioacids<sup>89</sup> and polysulphides of substituted thiurams<sup>90</sup> and of aryl isothiocyanates<sup>91</sup> as non-crystalline pitches.

Rubber-like materials have been made by the condensation of formaldehyde with solutions of alkali polysulphides. The resins formed could be milled, compounded, molded and vulcanized in the same manner as rubber.<sup>92</sup> The olefin-sulphide resins mentioned earlier in this chapter were also suggested as possible ingredients in aldehyde-polysulphide compositions. Patrick<sup>93</sup> replaced the aldehyde used in making the latter type of resin with hexamethylenetetramine or polymerized formaldehyde. The mixed aldehydes produced by oxidation of the gases formed in petroleum cracking have also been proposed.<sup>94</sup> In one example, the aldehydic mixture contained approximately 27 per cent formaldehyde, 3 per cent acetaldehyde and a considerable proportion of methanol and small quantities of higher aldehydes and acids. A sodium polysulphide solution was prepared by heating 40 g. of sodium hydroxide with 96 g. of sulphur and 150 g. of water. One hundred seventy g. of the mixed aldehydes were added to the polysulphide solution, and heat was applied to raise the temperature to the bubbling point. The mass was kept at incipient boiling for 4 hours and was then allowed to stand over night. The product after drying was a clear, soft, brownish resin. A variation of the procedure was to add an olefin halide to the aldehyde before reacting it with the polysulphide. A further modification of thioaldehyde resins is to incorporate a sulphur-phenol resin into polymethylene sulphide.<sup>95</sup>

Bruins<sup>96</sup> has prepared polythiofurfural in the following manner: A 3 per cent solution of furfural in water was treated with hydrogen sulphide for 3 hours at 50°C. The emulsion that resulted was coagulated by adding a small amount of hydrochloric acid, producing a rubber-like mass. When furfural is boiled with a solution of sodium polysulphide, a sticky material is formed which becomes firmer and more elastic on washing.<sup>97</sup> A further resinification of furfural is that which is effected by sulphur chloride. However, the resulting body is probably not a true thioaldehyde, since sulphuric and phosphoric acids are also said to produce the same substance.<sup>98</sup>

Dithiofuroic acid and its salts are said to be vulcanization accelerators. The acid has been prepared through the reaction of furfural and sulphuric acid on

<sup>87</sup> T. G. Levi, *Atti. accad. Lincei*, 1929, 9, 790; *Chem. Abs.*, 1929, 23, 5170.

<sup>88</sup> Methyl amine, hydrogen sulphide and formaldehyde react to form 3-methyl-1,3-thiazetamine,  $\text{CH}_3\text{-N} < (\text{CH}_2)_2 > \text{S}$ . C. G. LeFevre and R. J. LeFevre, *J.C.S.*, 1932, 1142.

<sup>89</sup> T. G. Levi, *Gazz. chim. ital.*, 1931, 61, 665, 803; *Chem. Abs.*, 1932, 26, 1250, 1902.

<sup>90</sup> T. G. Levi, *Gazz. chim. ital.*, 1931, 61, 373; *Chem. Abs.*, 1932, 26, 116.

<sup>91</sup> T. G. Levi, *Gazz. chim. ital.*, 1931, 61, 619; *Chem. Abs.*, 1932, 26, 702.

<sup>92</sup> J. Baer, *British P.* 298,889, 1928; *Brit. Chem. Abs. B*, 1929, 652. Swiss P. 132,322, 1927; *Chem. Abs.*, 1929, 23, 5062. German P. 530,163, 1928; *Chem. Abs.*, 1931, 25, 5311.

<sup>93</sup> J. C. Patrick, *Canadian P.* 336,070, 1933; *Chem. Abs.*, 1934, 28, 1823.

<sup>94</sup> Carleton Ellis, U. S. P. 1,964,725, July 3, 1934, to Ellis-Foster Co.; *Chem. Abs.*, 1934, 28, 5264.

<sup>95</sup> Carleton Ellis, U. S. P. 1,927,930, Sept. 26, 1933, to Ellis-Foster Co.; *Chem. Abs.*, 1933, 27, 5907.

<sup>96</sup> P. F. Bruins, *J.A.C.S.*, 1929, 51, 1270.

<sup>97</sup> J. C. Patrick, U. S. P. 1,996,487, Apr. 2, 1935.

<sup>98</sup> L. T. Richardson, U. S. P. 1,632,934, Sept. 4, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 3999.

aqueous sodium sulphide and sulphur.<sup>90</sup> Staudinger and Reichstein<sup>100</sup> allowed an alcoholic solution of furfural and ammonium acid sulphide to stand for several hours. When the initially formed bis(furylmethyl) disulphide was reduced, a small amount of resin was produced along with furylmethylthiol.

A viscous material results when rubber latex to which soluble sulphides or colloidal sulphur have been added is treated with aldehydes. The latter may either be in solution or in the vapor form. The product is vulcanized after shaping.<sup>101</sup> A similar composition, containing rubber latex, starch, sodium carbonate, a soluble metallic polysulphide and formaldehyde, has been used to render paper water- and grease-proof.<sup>102</sup>

A tanning agent has been made by condensing sulphonated cresol with the reaction product of urea, formaldehyde and ammonium sulphide. The final material had a  $p_H$  of about 5.<sup>103</sup> Urea condenses with thioaldehydes to form an "artificial albumin" from which molded objects have been made. Thus, an aqueous solution of ammonium sulphide (containing 20 g. of the dry salt) was poured on 100 g. of urea. The latter rapidly dissolved and 250 cc. of 40 per cent formaldehyde were added. A quiet reaction took place on heating, resulting in a syrup which, if the water was further evaporated, solidified on cooling to a glass-clear jelly.<sup>104</sup> In this case the sulphine syrup was soluble in water, but if larger proportions of formaldehyde were used the products were insoluble.<sup>105</sup> The latter bodies were liquids and did not solidify on standing. However, they were converted by acid anhydrides into clear, highly refractive solids which were further hardened by contact with warm air. The soluble type of product was rendered insoluble by evaporation or by coagulation with acids and alkalies. It was also produced in the cold by allowing the mixture to stand until a crystalline paste resulted. Contact with metals, especially aluminum, facilitated this conversion. In place of urea, its derivatives and analogues, e.g., guanidine and dicyanodiamide were also used.<sup>106</sup> Related plastic bodies have been made by condensing urea in alkaline solution with an aldehyde and a polysulphide, thiosulphate or polythionate.<sup>107</sup>

Hantzsch<sup>108</sup> reports that partial resmification of acetonyl thiocyanate<sup>109</sup> takes place when this substance is reacted with ammonia. An attempt has been made to determine the halogen in chloro- and bromoacetone by decomposing them with sodium sulphide and titrating the halogen. The method failed, the chief product being a resinous mass from which a little diacetonyl sulphide was isolated.<sup>110</sup>

<sup>90</sup> G. J. Leuck, U. S. P. 1,756,158, April 29, 1930, to Quaker Oats Co., *Chem. Abs.*, 1930, 24, 3022. Cf. the preparation of dithiobenzoic acid by the action of hydrogen persulphide on benzaldehyde in the presence of zinc chloride, I. Bloch, F. Höhn and G. Bugge, *J. prakt. Chem.*, 1910, (2) 82, 473; *J.C.S.*, 1911, 100 (1), 46. I. Bloch and G. Bugge, *ibid.*, 1910, (2) 82, 512; *J.C.S.*, 1911, 100 (1), 60.

<sup>100</sup> H. Staudinger and T. Reichstein, U. S. P. 1,715,795, June 4, 1929, to Int. Nahrungs- & Genussmittel A.-G.; *Chem. Abs.*, 1929, 23, 3715. Canadian P. 283,765, 1928; *Chem. Abs.*, 1928, 22, 4537.

<sup>101</sup> H. Reitz, German P. 453,899, 1923; *Brit. Chem. Abs. B*, 1929, 566.

<sup>102</sup> A. Ruderman, U. S. P. 1,723,581, Aug. 6, 1929; *Brit. Chem. Abs. B*, 1929, 811.

<sup>103</sup> German P. 562,826, 1930, to Soc. anon. Progil; *Chem. Abs.*, 1933, 27, 1231.

<sup>104</sup> British P. 313,455, 1928, to Pfenning-Schumacher-Werke G.m.b.H.; *Chem. Abs.*, 1930, 24, 1189.

See also French P. 767,899, 1934, to DuPont Viscoloid Co.; *Chem. Abs.*, 1935, 29, 524.

<sup>105</sup> British P. 366,009, 1929, addn. to 313,455, 1928, to Pfenning-Schumacher-Werke G.m.b.H.; *Chem. Abs.*, 1933, 27, 2002.

<sup>106</sup> British P. 366,065, 1929, addn. to 313,455, 1928, to Pfenning-Schumacher-Werke G.m.b.H.; *Chem. Abs.*, 1933, 27, 2002.

<sup>107</sup> I. Kreidl, British P. 416,661, 1932; *Brit. Chem. Abs. B*, 1934, 1022.

<sup>108</sup> A. Hantzsch and H. Schwaneberg, *Ber.*, 1928, 61, 1776; *Chem. Abs.*, 1929, 23, 101. See also A. Hantzsch, H. Schwedler and H. Schwaneberg, *ibid.*, 1927, 60, 2537; *Brit. Chem. Abs. A*, 1928, 187.

<sup>109</sup> See Chapter 31 for resins from ammonium thiocyanate and formaldehyde.

<sup>110</sup> A. J. P. Hoogveen and M. P. J. M. Jansen, *Rec. trav. chim.*, 1932, 51, 260; *Chem. Abs.*, 1932, 26, 2416.

## Chapter 59

### Sulphur-Phenol and Sulphur-Aniline Resins

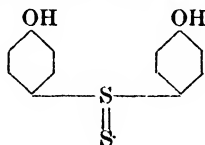
Sulphur and reagents furnishing it react with a wide variety of organic compounds. In the case of aromatic hydrocarbons many of the sulphur derivatives so obtained are dyes possessing high molecular weights and non-crystalline structures.<sup>1</sup> On the other hand, phenol forms resinous products not exhibiting the properties of dyestuffs when treated with sulphur or its compounds.<sup>2</sup> Some of the phenol-sulphur bodies have been adapted for molding while others serve as mordants and tanning agents. In spite of their complexity, an insight as to the constitution of these resins may be gained by a consideration of the simpler compounds isolated during the course of the sulphur-phenol reaction.

#### PHENOL-SULPHUR HALIDE RESINS

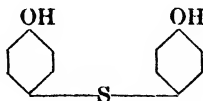
In 1887, Tassinari<sup>3</sup> reported that the violence of the reaction between phenol and sulphur dichloride made it necessary to dilute the reactants with carbon disulphide and to admix them slowly while cooling. After each addition of sulphur dichloride, the mixture became black but decolorized on standing. A compound, proved to be bis(p-hydroxyphenyl) sulphide, and a resin were isolated from the reaction products. The sulphide was accounted for by representing (empirically) the course of interaction as:



Tassinari concluded that hydrogen was not eliminated from the benzene nucleus inasmuch as acetylated phenol would not react with sulphur dichloride. Hence, he postulated the formation and rearrangement of an unstable intermediate,  $(\text{C}_6\text{H}_5\text{O})_2\text{S}$ . Tassinari also believed the resin to be of the general structure:



for on reduction with hydrogen, it was converted to the corresponding hydroxy thioether,



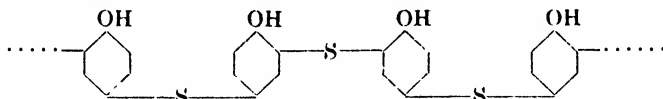
<sup>1</sup> A. Wahl, "The Manufacture of Organic Dyestuffs," Transl. by F. W. Atack, G. Bell & Sons, Ltd., London, 1914. O. Lange, "Die Schwefelfarbstoffe," 2nd. Ed., Leipzig, 1925. For the preparation of dyes from hydrocarbons and sulphur, see D. G. Palmer and S. J. Lloyd, *J.A.C.S.*, 1930, 52, 3338. A review of the action of sulphur on different types of hydrocarbons is given by Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, 430.

<sup>2</sup> German P. 102,897, 1895, to Farbenfabr. vorm. F. Bayer & Co.; *Chem. Zentr.*, 1899, 2, 352.

<sup>3</sup> G. Tassinari, *Gazz. chim. ital.*, 1887, 17, 83, 90; *J.C.S.*, 1887, 52, 807.

with the liberation of hydrogen sulphide. Resins were produced with other phenols (p-bromophenol, trichlorophenol and the cresols).  $\beta$ -Naphthol showed more violence in its reaction than  $\alpha$ -naphthol.

In view of the isolated intermediates, it is possible to consider the structure of the phenol-sulphur halide resins as a union of hydroxyphenyl radicals connected through sulphur atoms in the following manner:



Union of phenol nuclei, through sulphur atoms, entirely at ortho positions is not precluded, however. Furthermore, as each of the phenol nuclei has unsubstituted positions (ortho or para), molecular enlargement may also occur by replacing further hydrogen atoms.<sup>4</sup>

**Preparation of Phenol-Sulphur Chloride Resins.** Kuhn,<sup>5</sup> working in the author's laboratory, prepared an alcohol-soluble sulphur resin from "metaparacresol" (commercial cresol) and sulphur chloride. As this product may be regarded as typical of the general class of phenol-sulphur chloride resins, its preparation will be described in rather full detail.

A good quality of "metaparacresol" (1 part by weight) is diluted with an equal volume of toluene and stirred while 1.5 parts of sulphur chloride are added slowly. Hydrogen chloride is given off copiously, and the operation should therefore be carried on under a hood or in an apparatus equipped with absorption media. Heat is evolved during the course of the reaction, and at the end the hot product is blown with air at about 150°C. This treatment removes the solvent (which can be recovered) and also tends to deodorize the resin.

Removal of the odor is usually necessary, since the products contain traces of chlorophenols and other bodies possessing what would popularly be termed a "chemical smell" distasteful to non-chemists. At 150°C. the time required for the air-blowing is 15-30 minutes. A variant of this procedure involves blowing with steam at 120°C. and then baking in thin layers at 125°C. for several hours.<sup>6</sup> The resin is thus hardened somewhat and thoroughly dried. The latter condition is desirable since otherwise solutions of the resin in alcohol and other organic solvents are prepared with difficulty.

As the required initial materials when obtained commercially are not water-white, the resin produced by the action of sulphur chloride on phenols is likely to be colored. Moreover, more or less highly colored by-products are formed. Removal and avoidance of discoloration may be attained by the use of pure reagents, diluents and bleaching compounds. As a further precaution, the reaction vessels should be made of glass, enamelled iron or other substance incapable of contaminating the resin with a colored sulphide. Ellis and Meigs<sup>7</sup> purified their reactants by redistillation and then decolorized with fuller's earth or bone black. Since some color always results even with refined phenol and sulphur chloride, a limited amount of diluent is added to moderate the reaction. Large proportions of diluent tend to decrease the hardness of the resin. Specifically, 300 parts of phenol crystals are dissolved in 250 parts of benzene and a solution of sulphur monochloride (250 parts in 350 parts of benzene) is added slowly with

<sup>4</sup> R. Lesser and G. Gad (*Ber.*, 1923, 56, 963; *Chem. Abs.*, 1923, 17, 3181) observed that when the para position in a phenol is filled and one of the ortho positions has a negative substituent, no reaction takes place with sulphur mono- or dichloride.

<sup>5</sup> J. R. Kuhn, U. S. P. 1,564,002, Dec. 1, 1925, to Carleton Ellis; *Chem. Abs.*, 1926, 20, 513.

<sup>6</sup> Carleton Ellis, U. S. P. 1,557,519, Oct. 13, 1925; *Chem. Abs.*, 1926, 20, 118.

<sup>7</sup> Carleton Ellis and J. V. Meigs, U. S. P. 1,756,818, Apr. 29, 1930, to Carleton Ellis; *Chem. Abs.*, 1930, 24, 3092.



stirring. A creamy-white, bulky precipitate is formed which yields, when dried and pressed, a white, waxy material soluble in alcohol, aqueous sodium hydroxide and hot sodium carbonate solutions.

Water was found to be a satisfactory diluent by Ellis and Meigs.<sup>a</sup> It prevents excessive temperature rises, absorbs the hydrogen chloride formed (thus eliminating the necessity for external absorption apparatus) and seems to produce tougher resins than those given with other diluents. Sulphur monochloride (675 g.) is slowly run into an emulsion of 500 g. of cresol (97 per cent tar acids) in 2500 cc. of water and 300 g. of crushed ice. The resin precipitates as a yellow mass leaving a solution of hydrochloric acid as a by-product. After kneading with hot water, cooling, powdering and drying at 70-80°C., the solid material is largely soluble in alcohol, partly soluble in benzene or cold aqueous sodium hydroxide but dissolves completely in hot caustic soda solution. The resin, however, is unstable to heat, and the acid (which tends to discolor the product) must be removed. Strong bases are not satisfactory, but repeated extractions with a 3 per cent sodium carbonate solution give a stable resin. Calcium carbonate, freed from sodium hydroxide and other strong alkalies, may be employed. Zinc oxide also may serve as an antacid since in this case no undesirable by-products are formed. Iron oxide gives rise to highly colored areas which impair the appearance of the resin. Zinc oxide may be added while the crude resin (immediately after formation) is being kneaded with water or it may be added to an alcohol solution of the partially acid-free and dried material.

If the cheaper grades of phenols, i.e., the commercial types of cresol containing about 25 per cent of tar acids, are to be used, a reducing agent is incorporated in the reaction mixture. Ellis and Meigs employed stannous chloride, sodium hyposulphite and zinc dust, the latter being especially effective. During treatment with finely-divided zinc, hydrogen was evolved and the resin separated was light-yellow in color.

The hardness of the bodies obtained in the phenol-sulphur chloride reaction depends on several variables. Harder resins are prepared by replacing phenol with cresol, using water as a diluent, and by employing higher proportions of sulphur chloride.<sup>b</sup> With organic diluents, softer materials result. It has been found that increase in hardness decreases the solubility, as is shown in Table 64.

TABLE 64.—*Properties of Certain Phenol-Sulphur Chloride Resins.*

Parts of S <sub>2</sub> Cl <sub>2</sub> per 100 of Phenol	Appearance	Solubility
100 . . . . .	Viscous liquid	Easily soluble in alcohols, acetone, ethyl and methyl acetate, benzene and its homologues.
150 . . . . .	Sticky solid	As above.
200 . . . . .	Solid	Less soluble in alcohol, still fairly soluble in esters.
250-300 . . . . .	Hard resins	Progressively less soluble.
300 . . . . .	Hard resin	Not readily soluble in denatured alcohol, soluble in alcohol-benzene, ethyl acetate-chlorobenzene and acetone-toluene mixtures.
350 . . . . .	Hard resin	As above.
400 . . . . .	Not as hard as with 350 parts	

The particular resins described in this table were made by running sulphur

<sup>a</sup> Carleton Ellis and J. V. Meigs, U. S. P. 1,756,810, Apr. 29, 1930, to Carleton Ellis; *Chem. Abs.*, 1930, 24, 3092. See also K. Daimler (German P. 389,360, 1921, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1924, 43, 800B) who used the products as tanning agents.

<sup>b</sup> F. E. Layman, L. T. Richardson and O. A. Cherry (U. S. P. 1,692,914, Sept. 4, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 3999) have hardened sulphur chloride-phenol resins by treating them with additional quantities of sulphur chloride.

chloride into molten phenol and were light-yellow to light-brown in color.<sup>10</sup> The softer members of the series have been suggested for use in the preparation of fly paper. Some of the products find application as tanning agents. In varnish-making, the resin derived from 1.33-1.50 parts of sulphur chloride per part of any of the lower phenols is recommended. For the latter purpose, a fairly light-colored and chemically inactive resin is required. A difficulty presents itself here, for the sulphur resins usually contain small quantities of hydrochloric acid which eventually lead to the corrosion of metallic surfaces. Neutralization with bases does not solve the problem since discoloration of the product ensues. Ellis<sup>11</sup> obviated these difficulties by replacing the hydrochloric acid with acetic acid through the addition of sodium acetate. The relatively weak organic acid volatilizes in use leaving the film sufficiently acid to remain light in color, but not enough to be objectionably corrosive. If pigments are to be used in the resin, zinc oxides, lithopone and barytes are preferable to lead compounds, since the latter become blackened through reaction with residual traces of sulphur.

Phenol-sulphur chloride resins have been applied to other purposes than in varnishes and as tanning agents. Ellis<sup>12</sup> employed this type of synthetic product to minimize the crystallizing tendency of sulphur. To achieve this end, crude xylol is dissolved in benzene and reacted with an equal weight of sulphur chloride. The resulting material, after being neutralized and deodorized as described previously, is added to three times its weight of melted sulphur. No indication of the crystalline structure common to sulphur is shown by the composition (which is also ignited with greater difficulty). The sulphur composition may be used to impregnate fiber board and also for molding.<sup>13</sup> A phenol-sulphur dichloride resin can be mixed with cellulose esters and ethers in the manufacture of lacquers, adhesives and yarn.<sup>14</sup> Phenol-sulphur chloride resins incorporated with equal parts of urea-formaldehyde condensation products yield a mixture which is readily fusible and gives a sharp imprint in a mold.<sup>15</sup> This type of composition can also be used as a binder for mica powder and other fillers. Guanidines and other urea derivatives may be substituted for urea in the blend. Inter-resinification, or reaction between the two types of resin, is considered to take place during the molding operation. This is probably due to condensation of phenol with formaldehyde from the urea resin.

Alone, sulphur resins may be employed as flotation reagents,<sup>16</sup> fungicides, tanning agents and rubber preservatives.<sup>17</sup> As the products retain their phenolic groups, they form metallic salts. The calcium, magnesium, zinc and copper salts are only slightly soluble in water and are described as particularly active in the destruction of the fungi *Oidium* and *Peronospera*.<sup>18</sup> Hilbert and Johnson<sup>19</sup> prepared hydroxyphenyl sulphides possessing germicidal properties. The method consists of diazotizing an aromatic amine and condensing with, e.g., the sodium salt of p-methoxythiophenol. On heating, the reaction product decomposes forming p-methoxydiphenyl sulphide which on hydrolysis gives p-hydroxydiphenyl sulphide:

<sup>10</sup> Carleton Ellis, U. S. P. 1,663,160, Mar. 20, 1928; *Chem. Abs.*, 1928, 22, 1696.

<sup>11</sup> Carleton Ellis, *loc. cit.*

<sup>12</sup> Carleton Ellis, U. S. P. 1,835,766 and 1,835,767, Dec. 8, 1931; *Chem. Abs.*, 1932, 26, 1123 U. S. P. 1,690,335, Nov. 6, 1928; *Chem. Abs.*, 1929, 23, 533

<sup>13</sup> See Chapter 57 for a further discussion of the uses to which plastic sulphur is applied.

<sup>14</sup> British P. 417,944, 1932, to British Celanese, Ltd.; *Brit. Chem. Abs.*, B, 1935, 34.

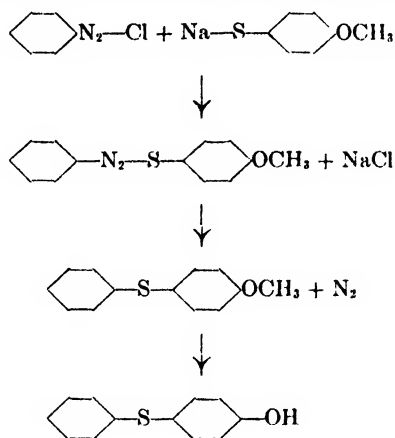
<sup>15</sup> Carleton Ellis, U. S. P. 1,897,978, Feb. 14, 1933, to Ellis-Forster Co.; *Chem. Abs.*, 1933, 27, 2831 See also Chapter 32.

<sup>16</sup> F. G. Moses and E. J. Canavan, U. S. P. 1,912,588, June 6, 1933, to Barrett Co.; *Chem. Abs.*, 1933, 27, 4204.

<sup>17</sup> British P. 359,045, 1920, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 445.

<sup>18</sup> German P. 364,848 and 364,849, 1920, to Farb. vorm. Meister, Lucius & Brühning; *J.S.C.I.*, 1923, 42, 289A.

<sup>19</sup> G. E. Hilbert and T. B. Johnson, *J.A.C.S.*, 1929, 51, 1526. See also T. B. Johnson, U. S. P. 1,976,732, Oct. 16, 1934, to Sharp & Dohme, Inc.; *Chem. Abs.*, 1934, 28, 7432.



The phenol coefficient (amount of dilution necessary to give the same bactericidal activity as phenol) of p-hydroxydiphenyl sulphide was 115. Tests on rabbits indicated the compound was relatively non-toxic.

Kartaschoff<sup>20</sup> prepared metal derivatives by treating intermediates of the sulphur chloride-phenol reaction with salts of tin, chromium, antimony, zinc, molybdenum, aluminum, manganese or nickel. Tin chloride, however, is the principal reagent. The condensation products possess tanning properties.

**Modifications of the Phenol-Sulphur Halide Resins.** Daimler<sup>21</sup> employed a phenol sulphonic acid in the reaction with sulphur chloride. A solution of the product can be used as a tanning agent. Phenol-sulphur halide resins were sulphonated by Virck<sup>22</sup> in conjunction with an excess of a phenol. The sulphur chloride-phenol resin is treated with concentrated sulphuric acid at 100°C., the temperature is raised to 220°C. and a further proportion of a phenol is incorporated. Excess phenol is expelled *in vacuo* at 240°C. The product is soluble in aqueous sodium carbonate and is precipitated as colorless flakes by acids. Resins of this type may be utilized in the manufacture of lakes with basic dyestuffs. In an earlier method, Virck<sup>23</sup> omitted the addition of phenol during sulphonation. A procedure analogous to the treatment with sulphuric acid is acylation of the resin (during its formation) with acetic anhydride or benzoyl chloride.<sup>24</sup>

Sulphur halides other than the mono- and dichloride also give resins on reaction with phenols. As an example, 2 mols of thionyl chloride are added at 0°C. to a solution of 1 mol of technical cresol in an equal weight of concentrated sulphuric acid.<sup>25</sup> The mixture is poured on ice, and the precipitate formed is separated and heated giving a high-melting, ruby-colored resin soluble in alcohol and aqueous sodium carbonate. McMaster and Ahmann<sup>26</sup> obtained glassy solids of indefinite composition by the action of thionyl chloride with m-hydroxybenzoic acid or with o- and m-cresotinic acids.

<sup>20</sup> V. Kartaschoff, U. S. P. 1,989,989, Feb. 5, 1935, to Chem. Fabr. vorm. Sandoz, *Chem. Abs.*, 1935 29, 1999. British P. 382,333, 1932, addn. to 365,534; *Chem. Abs.*, 1933, 27, 4244.

<sup>21</sup> K. Daimler, German P. 389,360, 1921, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1924, 43, 800B.

<sup>22</sup> P. Virck, U. S. P. 1,736,063, Nov. 19, 1929, to General Aniline Works; *Chem. Abs.*, 1930, 24, 698. British P. 242,974, 1925, addn. to 232,958, 1925, to A.-G. f. Anilin-Fabr.; *Brit. Chem. Abs. B.*, 1926, 596.

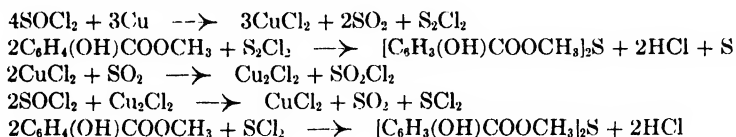
<sup>23</sup> P. Virck, U. S. P. 1,553,014, Sept. 8, 1925, to A.-G. für Anilin-Fabr.; *Chem. Abs.*, 1925, 19, 3599. British P. 232,958, 1925; *J.S.C.I.*, 1925, 44, 956B.

<sup>24</sup> German P. 425,798, 1924, addn. to 418,498, 1923, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs. B.*, 1926, 596.

<sup>25</sup> German P. 362,353, 1920, to Farb. vorm. Meister, Lucius & Brünig; *J.S.C.I.*, 1923, 42, 613A. See also Carleton Ellis and J. V. Meigs, U. S. P. 1,756,818, Apr. 29, 1930, to Carleton Ellis; *Chem. Abs.*, 1930, 24, 3092.

<sup>26</sup> L. McMaster and F. F. Ahmann, *J.A.C.S.*, 1928, 50, 145.

According to the work of Hirwe, Jadhav and Chakradeo,<sup>27</sup> hydroxybenzoic acids do not condense readily with thionyl chloride. The presence of a carboxyl group introduces the possibility of forming different anhydro compounds and inhibits the reaction. The difficulties are avoided by employing an ester (such as methyl salicylate) and finely divided copper. The reactions involved in the condensation of methyl salicylate are reported to be as follows:



It is interesting to note that the thionyl chloride is reduced to sulphur monochloride and dichloride before taking part in the reaction. The main reaction product, bis(3-carbomethoxy-4-hydroxy-phenyl) thioether is analogous to the phenol-sulphur halide intermediates.

The properties of sulphur-halide resins may be modified by the addition of various substances in the preparation of compositions to fit particular needs. Votapek<sup>28</sup> mixed the resin with stearin pitch and asbestos to form a molding composition. To 100 parts of a mixture including stearin pitch, coal-tar pitch, gilsonite, castor oil and benzene as modifiers, Cherry and Chosa<sup>29</sup> added 1 part of phenol and 1 part of sulphur chloride. Mordants and wool-resists used in dyeing can be made by incorporating a mixture of sulphur monochloride (5 parts) and stannous chloride (2 parts) with phenol (5.4 parts) at 50-100°C.<sup>30</sup> A 35 per cent solution of sodium hydroxide (10 parts) is stirred in at the end of the reaction. Layman and Richardson<sup>31</sup> prepared sound records from a composition made by heating 10 parts of phenol-sulphur chloride resin and 1 part of white lead at 150°C.

**Use of Formaldehyde as a Modifier.** Modification of phenol-sulphur halide resins with formaldehyde follows two general courses. The aldehyde may be added to the final resin, mainly as a hardening agent; or the phenol used in the initial reaction may be partially condensed with formaldehyde and subsequently treated with sulphur chloride. McCoy<sup>32</sup> found that the resinous substance formed by the action of sulphur chloride on a phenol in carbon tetrachloride solution is solidified when dissolved in phenol and heated with formaldehyde. Phenol may be mixed with fatty oils and then treated with sulphur chloride and formaldehyde.<sup>33</sup> In a related procedure, the sulphur halide resin is incorporated with formaldehyde, cyclohexylamine and beeswax to prepare a shellac substitute.<sup>34</sup>

Ellis<sup>35</sup> observed that the addition of 3 per cent of paraform, hexamethylenetetramine or formaldehyde was sufficient to raise the softening point of a phenol-sulphur chloride resin about 28°C. and that further amounts conferred no beneficial effects. The compositions containing paraform are lighter in color than those with hexamethylenetetramine. In preparing molding materials, the filler may be impregnated with a resin solution, the solvent removed by evaporation and the product

<sup>27</sup> N. W. Hirwe, G. V. Jadhav and Y. M. Chakradeo, *J.A.C.S.*, 1935, 57, 101.

<sup>28</sup> G. J. Votapek, U. S. P. 1,574,771, Mar. 2, 1926, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1926, 20, 1500.

<sup>29</sup> O. A. Cherry and C. F. Chosa, U. S. P. 1,678,635, July 31, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 3747.

<sup>30</sup> British P. 393,011, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1933, 778.

<sup>31</sup> F. E. Layman and L. T. Richardson, U. S. P. 1,682,913, Sept. 4, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 3966.

<sup>32</sup> J. P. A. McCoy, U. S. P. 1,194,201, Aug. 8, 1916; *Chem. Abs.*, 1916, 10, 2534. British P. 13,657, 1913; *J.S.C.I.*, 1914, 33, 653. See also J. J. Buser, French P. 458,904, 1913; *J.S.C.I.*, 1913, 32, 1163.

<sup>33</sup> For the reaction of sulphur chloride on fatty oils to form factice, see Chapter 60.

<sup>34</sup> British P. 221,205, 1924, to Soc. anon. pour l'ind. chim. à Bâle; *Brit. Chem. Abs.* B, 1926, 67. See also *Farbe u. Lack*, 1927, 21, 286; *Chem. Abs.*, 1928, 22, 3055.

<sup>35</sup> Carleton Ellis, U. S. P. 1,787,618, Jan. 6, 1931; *Chem. Abs.*, 1931, 25, 835.

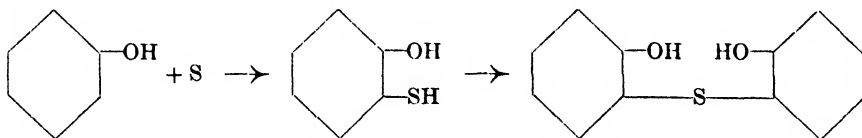
powdered. To illustrate, a resin (100 parts) derived from "metaparacresol" and sulphur chloride is dissolved in 200 parts of denatured alcohol with 3 parts of stearic acid (serving as a mold lubricant). A solution of 6 parts of hexamethylenetetramine in 100 parts of denatured alcohol is mixed with 100 parts of wood flour and evaporated. The resulting material is incorporated with the resin solution forming a paste that is dried for about 3 hours at 100°C. and powdered for molding. As the formaldehyde does not make the resins infusible but merely raises their softening points, the finished article may be broken up if defective and molded again.

The action of sulphur chloride on phenol-formaldehyde resins has been especially studied by Samuel<sup>36</sup> who was interested in the production of heat- and electrical-insulators. This investigator prepared a partially condensed product from cresol and formaldehyde which was still soluble in alcohol and acetone. To the condensate was then added as much sulphur monochloride as would continue to react. The evolved hydrogen chloride had to be neutralized to prevent further polymerization of the phenol-formaldehyde resin. The final product contained about 12 per cent of sulphur and was soluble in alcohol, acetone, hydrocarbon solvents and pyridine. When heated to 80°C. the resin softened, and at 150°C. it polymerized rapidly to a hard, infusible mass insoluble in all the ordinary solvents. The hardened resin possessed a high dielectric constant, its resistance being given as  $300 \times 10^6$  megohms per centimeter. Samuel named the resin "Thiolite" and used the unpolymerized form in thermosetting molding compositions.<sup>37</sup> Solutions of the partially condensed product have also been used as coating and impregnating agents.<sup>38</sup> The resin is heated, after the solvent evaporates, to convert it into a hard and infusible mass.

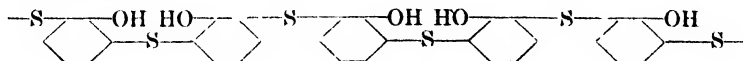
#### PHENOL-SULPHUR RESINS

Phenol and sulphur form, under certain conditions, resins having diverse applications as in molding, tanning and in the dyeing industry. In general, though differing in preparation the phenol-sulphur resins closely resemble the phenol-sulphur halide products previously described.

In the initial interaction of sulphur and phenol, o-hydroxybenzenethiol is probably first formed and oxidized by the excess sulphur to o,o'-dihydroxydiphenyl sulphide.<sup>39</sup>



As in the sulphur-halide reaction, the phenol nucleus retains unreplaced hydrogen atoms in the ortho and para positions. Hence, the molecule may branch out on these positions also:



<sup>36</sup> A. A. Samuel, *Compt. rend.*, 1926, 182, 207; *Plastics*, 1927, 3, 13; *Chem. Abs.*, 1926, 20, 2712. *Ind. Eng. Chem., News Ed.*, 1926, 4 (6), 7. U. S. P. 1,704,629, Mar. 5, 1929, and 1,770,663, July 15, 1930; *Chem. Abs.*, 1929, 23, 1971; 1930, 24, 4563. French P. 549,811, and 693,730, 1929; *Chem. Abs.*, 1931, 25, 1692. French P. 692,912, 1929, to Soc. Levy, Samuel & Levy; *Chem. Abs.*, 1931, 25, 1692.

<sup>37</sup> Cf. R. A. L. Volet, French P. 633,537, 1927; *Chem. Abs.*, 1928, 22, 3500.

<sup>38</sup> L. Levy, British P. 273,756, 1926; *Chem. Abs.*, 1928, 22, 2071.

<sup>39</sup> R. Möhlau, *Chem.-Ztg.*, 1907, 31, 936. B. Holmberg, *Ber.*, 1910, 43, 220; *J.C.S.*, 1910, 98 (1), 150. L. Hattinger, *Monatsh.*, 1883, 4, 165; *J.C.S.*, 1883, 44, 988. F. Krafit and R. E. Lyons, *Ber.*, 1896, 29, 435; *J.C.S.*, 1896, 70 (1), 297.

It is possible, moreover, for each of the sulphur linkages to take up more sulphur giving polysulphides of greater complexity than the products of the phenol-sulphur halide reaction.

More complex phenols give analogous reactions with sulphur. Thus, Lefevre and Desgrez<sup>40</sup> obtained 2,4,2'-trihydroxybenzophenone-5,5'-disulphide from 2,4,2'-trihydroxybenzophenone and sulphur. In a similar manner, the disulphides of 2,4,2'-trihydroxybenzosulphone, 3-hydroxy-3'-aminobenzosulphone and 2,2'-dihydroxydiphenylamine can be prepared.

**Preparation of Phenol-Sulphur Resins.** A relatively simple procedure for the preparation of phenol-sulphur resins was developed by Canavan.<sup>41</sup> Tar acids (crude mixture of phenols) are heated in an autoclave with sulphur. Part of the hydrogen sulphide evolved during the reaction is allowed to escape, maintaining a pressure of 50 lbs. per square inch. The most efficient temperature for the process is stated to be 230°C. The resin may be used as a flotation reagent according to Canavan.

The majority of investigators in the phenol-sulphur resin field have employed catalysts (usually bases) to hasten production. Ellis<sup>42</sup> heated 50 parts of phenol with 80 parts of sulphur and 1-10 parts of potassium carbonate for 4 hours at a temperature of 135-140°C. The temperature was then raised to 160°C. for another 4-hour period, resulting in the formation of a hard resin that liquefied slowly at 130-140°C. Higher proportions of sulphur increased the melting point of the product. Since the resin was intended for use in molding compositions, retention of the base employed as catalyst was undesirable, for subsequent decomposition with the liberation of hydrogen sulphide would occur. To remove the carbonate, the pulverized resin was washed or dissolved in alkali and precipitated with acid.

A non-dyeing sulphur-phenol composition, described by Downing, Clarkson and Hannum,<sup>43</sup> was prepared by employing a limited proportion of sulphur insufficient to react with all the phenol. Sodium phenolate is first formed by heating 376 g. of phenol and 40 g. of powdered sodium hydroxide at 180°C. To the molten mass, 160 g. of sulphur are added, and the mixture is heated at 182°C. until the evolution of hydrogen sulphide ceases. Unreacted phenol is removed by steam distillation, and the resin is cooled and powdered. Dissolved in water with the aid of sodium carbonate, the resin gives a greenish-brown solution that confers on cloth great affinity for basic dyes.

Like the phenol-sulphur halide products described earlier in this chapter, the phenol-sulphur resins decrease in solubility as the sulphur content increases. Blumfeldt<sup>44</sup> obtained resins soluble in alcohol, acetone and alkalis by restricting the amount of alkali to less than 0.2 the equivalent of the phenol and using only 2-3 mols of sulphur per mol of phenol. On molding, these resins become hard and insoluble, and they are suggested as substitutes for the more expensive Bakelite types. The phenol-sulphur resins may be hardened by the addition of formaldehyde or hexamethylenetetramine.

Resins, derived from phenol and sulphur, with large proportions of alkali have been used as mordants<sup>45</sup> for dyes and as coloring matters by themselves.<sup>46</sup> One

<sup>40</sup> C. Lefevre and C. Desgrez, *Compt. rend.*, 1934, 199, 300; *Chem. Abs.*, 1934, 28, 6709

<sup>41</sup> E. J. Canavan, U. S. P. 1,828,172, Oct. 20, 1931, to Barrett Co.; *Chem. Abs.*, 1932, 26, 682.

<sup>42</sup> Carleton Ellis, U. S. P. 1,636,596, July 19, 1927; *Chem. Abs.*, 1927, 21, 2993. U. S. P. 1,690,160, Nov. 6, 1928; *Chem. Abs.*, 1929, 23, 533.

<sup>43</sup> F. B. Downing, R. G. Clarkson and C. W. Hannum, U. S. P. 1,985,602, Dec. 25, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1935, 29, 1101.

<sup>44</sup> A. E. Blumfeldt, U. S. P. 1,435,801, Nov. 14, 1922; *Chem. Abs.*, 1923, 17, 477. British P. 186,107, 1921, to Soc. anon. pour l'ind. chim. & Bâle; *Chem. Abs.*, 1923, 17, 345. Swiss P. 92,408, 105,855, 105,856, 105,857 and 105,858, 1922; *Brit. Chem. Abs. B*, 1926, 203. Swiss P. 95,180, 1922, addn. to 92,408.

<sup>45</sup> Dutch P. 19,063, 1928, to N. V. Fabriek van Chemische Producten; *Chem. Abs.*, 1929, 23, 1758.

<sup>46</sup> A. Weinberg, U. S. P. 596,559, Jan. 4, 1898, to L. Cassella & Co. R. Demuth, U. S. P. 608,755, May 10, 1898, to Farbenfabr. vorm. F. Bayer & Co.

method for the preparation of mordants employs only 0.6 per cent of sodium hydroxide in a melt of phenol and sulphur, but the resulting mass is cooled, ground with a further 25 per cent of sodium hydroxide and fused before use.<sup>47</sup>

A modification of the general procedure consists in refluxing a solution of phenol in caustic alkali with sulphur.<sup>48</sup> Instead of using sodium or potassium hydroxide, Bergdolt and Ballauf<sup>49</sup> catalyzed the reaction with a solution of an alkali-metal carbonate. Thauss<sup>50</sup> recommends substituting sodium formate for sodium hydroxide as the catalyst.



FIG. 163.

Cupboard in One of the Author's Laboratories. This was varnished with a sulphur-phenol resin composition over 15 years ago. Finish is still in good condition.

Battegay<sup>51</sup> stated that alkali hydroxides tended to give poor yields of phenol-sulphur resins which, furthermore, were lacking in uniformity. This observer suggested that a small amount of iodine be utilized in place of alkali. The initial interaction with iodine as catalyst is reported to form iodophenol which on dissociation facilitates the resin-forming reaction. Compounds of aluminum and antimony together with hydrogen fluoride have also found use in the preparation of resins from phenols and sulphur.<sup>52</sup>

Besides their application in molding and in dyeing cotton, the sulphur-phenol resins have been utilized to protect animal fibers from the action of alkaline

<sup>47</sup> M. L. Crossley and M. L. Dolt, U. S. P. 1,882,777, and 1,882,778, Oct. 18, 1932, to Calco Chem. Co., Inc.; *Chem. Abs.*, 1933, 27, 851.

<sup>48</sup> A. Thauss and A. Günther, U. S. P. 1,450,463, Apr. 3, 1923, to Farbenfabr. vorm. F. Bayer & Co.; *Chem. Abs.*, 1923, 17, 1893. British P. 173,313, 1920; *J.S.C.I.*, 1922, 41, 139A. U. S. Reissue 17,940, Jan. 27, 1931, to General Aniline Works; *Chem. Abs.*, 1931, 25, 1262. See also N. V. Filippov, Russian P. 13,094, 1924, to Pravlenie Ivanovo-Voznesenskogo Tekstilnogo Tresta; *Chem. Abs.*, 1933, 27, 3832. S. F. Karats and P. V. Khudyakov, Russian P. 38,199, 1927, addn. to 13,094, 1924; *Chem. Abs.*, 1933, 27, 3833.

<sup>49</sup> A. Bergdolt and F. Ballauf, U. S. P. 1,922,467, Aug. 15, 1933, to General Aniline Works; *Chem. Abs.*, 1933, 27, 5197.

<sup>50</sup> A. Thauss, U. S. P. 1,757,400, May 6, 1930, to General Aniline Works; *Chem. Abs.*, 1930, 24, 3361. British P. 298,280, 1927, addn. to 173,313, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1928, 836.

<sup>51</sup> M. Battagay, U. S. P. 1,533,340, Jan. 13, 1925; *Chem. Abs.*, 1925, 19, 899. Cf. U. S. P. 1,686,324, Oct. 2, 1928, to Calco Chem. Co.; *Chem. Abs.*, 1928, 22, 4533.

<sup>52</sup> French P. 650,814, 1923, to Soc. anon. pour l'ind. chim. & Saint-Denis; *Chem. Abs.*, 1929, 23, 3356.

liquids,<sup>65</sup> to diminish the tendency of hydrated cellulose to swell<sup>66</sup> and in the dyeing of rubber.<sup>66</sup>

**Modified Sulphur-Phenol Resins.** During discussion of the phenol-sulphur chloride resins, the preparation of mordants by the addition of tin compounds was noted. Muth<sup>66</sup> similarly treated bodies obtained from phenols and sulphur. Thus, the sulphur-phenol compositions are dissolved in aqueous alkali and heated with stannous chloride, potassium hexachlorostannate or sodium stannate. After heating, the resin-tin complex is isolated by acidifying or by evaporation. Some of the products possessed not only mordanting properties but were found to serve as wool-resists in dyeing mixed fabrics. Wool-reserving substances of the same general nature have been made by fusing sulphur-treated phenol with a phenol and sodium stannate.<sup>67</sup>

Leeman and Kartaschoff<sup>68</sup> prepared related mordanting, tanning and wool-reserving bodies by the action of sulphur on phenol in a water solution of an alkali hydroxide or carbonate together with ammonium molybdate, chromium acetate, tin chloride or aluminum sulphate. The alkali could be replaced by iodine or an alkali salt of a weak acid (e.g., sodium formate, mentioned previously).<sup>69</sup> Materials also proposed as tanning agents were developed by Kraus<sup>70</sup> using sulphur, phenols (especially naphthols), sodium sulphite and formaldehyde. As an example, 144 kg. of  $\beta$ -naphthol, 100 l. of water, 20 kg. of sodium hydroxide and 80 kg. of powdered sulphur are refluxed for 40-80 hours and then diluted with 250 l. of water. On cooling, 250 kg. of crystallized sodium sulphite and 80 kg. of 40 per cent formalin are incorporated with the solution. The final liquid becomes entirely clear after standing for some time at 70-80°C., and subsequent to neutralization is ready for use as a tanning reagent. Schütte<sup>71</sup> varied the procedure by reacting the phenol first with formaldehyde and sodium sulphite and then treating the resulting product with sulphur and alkali. The tanning reagents can be mixed in the dry state with solid acids so that their solutions will have the requisite acidity.<sup>72</sup>

Daimler<sup>73</sup> proposed the reaction of sulphur and alkali with phenolic resins. The products, in the form of alkali salts, are soluble but precipitate on the addition of acids. The material formed by heating an aldehyde-phenol condensate with iodine and sulphur may be employed as a rubber anti-oxidant.<sup>74</sup>

Resins, soluble in alcohol and acetone, produced by the reaction of phenol and sulphur in the presence of limited amounts of alkali were modified by Blumfeldt<sup>75</sup> with acetic anhydride. The resin is heated with the acetylating agent at 150-180°C. until no longer soluble in alcohol. After distilling off excess acetic anhy-

<sup>65</sup> British P. 238,857, 1925, to A.-G. f. Anilin-Fabrik.; *J.S.C.I.*, 1925, 44, 879B.

<sup>66</sup> British P. 278,684, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 242. French P. 653,817, 1928; *Chem. Abs.*, 1929, 23, 3807.

<sup>67</sup> S. A. Blinkov, S. I. Apevalkin and A. G. Menga, Russian P. 23,342, 1931; *Chem. Abs.*, 1932, 26, 1829.

<sup>68</sup> F. Muth, U. S. P. 1,911,709, May 30, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 5197. British P. 360,378, 1930; *Chem. Abs.*, 1933, 27, 1204.

<sup>69</sup> British P. 370,458, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 763.

<sup>70</sup> H. Leeman and V. Kartaschoff, U. S. P. 1,928,257, Sept. 26, 1933, to Chem. Fabr. vorm. Sandoz; *Chem. Abs.*, 1933, 27, 5753. French P. 704,635, 1930, 39,338 and 40,616, 1931; *Chem. Abs.*, 1931, 25, 4721, 1933, 27, 732, 1362.

<sup>71</sup> French P. 40,088, 1931, addn. to 704,635, to Chem. Fabr. vorm. Sandoz; *Chem. Abs.*, 1933, 27, 732.

<sup>72</sup> E. Kraus, U. S. P. 1,690,640 and 1,690,641, Nov. 6, 1928, to Fabrik van Chemische Producten; *Chem. Abs.*, 1929, 23, 395, 526. British P. 269,970 and 269,971, 1926; *Chem. Abs.*, 1928, 22, 1481.

<sup>73</sup> H. Schütte, U. S. P. 1,727,135, Sept. 13, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 5349. French P. 640,224, 1927; *Chem. Abs.*, 1929, 23, 1008.

<sup>74</sup> P. Virck and G. Matzdorf, German P. 495,338, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 3394. French P. 658,874, 1928; *Chem. Abs.*, 1929, 23, 5349.

<sup>75</sup> K. Daimler, German P. 409,789, 1921, addn. to 400,242, to Farbenfabr. vorm. F. Bayer & Co.; *J.S.C.I.*, 1925, 44, 461B.

<sup>76</sup> W. Scott, U. S. P. 1,773,379, Aug. 19, 1930, to Rubber Service Labs.; *Chem. Abs.*, 1930, 24, 5182.

<sup>77</sup> A. Blumfeldt, U. S. P. 1,588,439, June 15, 1926, to Soc. anon. pour l'ind. chim. & Bâle; *Chem. Abs.*, 1926, 20, 2589. British P. 203,310, 1923; *Chem. Abs.*, 1924, 18, 594.



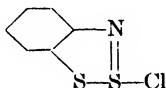
dride and the acetic acid formed in the reaction, the product is a light-yellow to brown powder soluble in acetone, cyclohexane, chloroform and ethylene chloride, but insoluble in alcohol and alkalis. Benzoyl, acetyl or p-toluenesulphonyl chloride may also be employed. The modified resins were said to resemble closely the natural resinotannol<sup>66</sup> esters and hence could be used in lacquers and as impregnants.

**Miscellaneous Sulphur-Phenol Resins.** Cherry<sup>67</sup> prepared resins by combining the action of sulphur and sulphur chloride on phenols. Specifically, 50 parts of sulphur are dissolved in 200 parts of sulphur monochloride and the solution added slowly to 100 parts of phenol. The resulting composition is said to be satisfactory when used in molding. Analogous products in which sulphur is replaced by selenium were also investigated by Cherry. Selenium oxychloride and its reaction with phenols have been studied by Morgan and Burstall.<sup>68</sup> With phenol itself, there are produced initially two isomeric selenonium chlorides of the type  $[(HO-C_6H_4)_2Se] Cl$ . The more soluble of the two is obtained as a gum setting to a glassy mass when kept over sulphuric acid. Cresol gives, in addition to the selenonium chloride derivative, a small amount of bis(4-hydroxy-3-methylphenyl) selenide and gummy by-products. According to Meyer and Wagner,<sup>69</sup> selenic acid when poured on well-cooled phenol and diluted with water gives a light-brown precipitate that cannot be crystallized. In contrast with the reaction of sulphuric acid and phenol, no phenolselenonic acid can be isolated.

Condensation products of formaldehyde and naphthalene sulphonic acids (described in Chapter 12) react with hydroxyaromatic alcohols to give tanning agents and resists used in the dyeing of animal fibers.<sup>70</sup> Resinous substances are obtained by the action of aluminum sulphide<sup>71</sup> and chlorosulphonic acid<sup>72</sup> on phenol at temperatures below the latter's boiling point.

#### AROMATIC AMINES AND SULPHUR CHLORIDE

The mechanism of the action of sulphur halides on aromatic amines differs only slightly from that of phenols and sulphur halides (described earlier in this chapter). Hydrogen chloride splits out, but in some cases at least part of the hydrogen removed comes from the amino group. Herz,<sup>73</sup> employing a considerable excess of sulphur chloride with aniline hydrochloride, prepared a yellow crystalline substance to which the formula



was assigned. Other aromatic amines, their salts and acyl derivatives gave similar products (both in the dry state and in the presence of diluents) serving as dye intermediates. A related material from o-toluidine was proposed by Christmann<sup>74</sup> as a pickling inhibitor.

<sup>66</sup> Acyl derivatives of resin alcohols containing phenolic hydroxyl groups.

<sup>67</sup> O. A. Cherry, U. S. P. 1,616,741, Feb. 8, 1927, to Cutler-Hammer Mfg. Co., *Chem. Abs.*, 1927, 21, 996.

<sup>68</sup> G. T. Morgan and F. H. Burstall, *J.C.S.*, 1928, 3260. Cf. G. T. Morgan and H. Burgess (*J.C.S.*, 1929, 2214) for the reaction of basic tellurium chloride with the cresols. Other selenium resins are discussed in Chapter 62.

<sup>69</sup> J. Meyer and W. Wagner, *Ber.*, 1922, 55, 1216; *J.C.S.*, 1922, 122 (1), 620.

<sup>70</sup> British P. 251,294, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1927, 21, 1371.

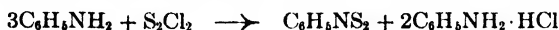
<sup>71</sup> G. R. Levy, *Atti Congr. Naz. Chim. Ind.*, 1924, 373; *J.S.C.I.*, 1925, 44, 263B.

<sup>72</sup> J. Pollak, E. Gebauer-Fülneegg, E. Blumenstock-Halward and E. Petertil, *Monatsh.*, 1928, 49, 187; *Chem. Abs.*, 1928, 22, 3652.

<sup>73</sup> R. Herz, U. S. P. 1,637,023, July 26, 1927 and 1,699,432, Jan. 15, 1929, to Grasselli Dyestuff Corp.; *Chem. Abs.*, 1928, 22, 1365; 1929, 23, 1140. See also W. König with P. Seidel and G. Stühmer, *Ber.*, 1928, 61, 2065; *Chem. Abs.*, 1929, 23, 389.

<sup>74</sup> L. J. Christmann, U. S. P. 1,734,561, Nov. 5, 1929, to American Cyanamid Co.; *Chem. Abs.*, 1930, 24, 330.

Coffey<sup>75</sup> found that with dilute solutions and low temperatures an excess of aniline reacts in the following manner:

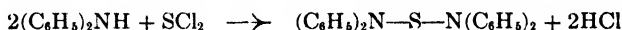


The product ( $\text{C}_6\text{H}_5\text{NS}_2$ ) was a thick orange-red oil which Coffey named N-dithiophenylamine. On standing the molecular weight of this compound increased indicating polymerization. The substance may be used as a vulcanizer for rubber, according to Whittelsey and Bradley.<sup>76</sup>

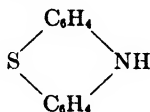
Merz and Schmidt<sup>77</sup> studied the action of several sulphur halides on aniline. With sulphur iodide at 160-170°C., thioaniline (bisaminophenyl sulphide) and a considerable quantity of a dark resinous body assumed to contain dithioaniline (bisaminophenyl disulphide) were obtained. Aniline and sulphur bromide with benzene as a diluent gave a resinous mass from which small quantities of dithioaniline and thioaniline could be extracted with acid. From sulphur chloride and aniline, a resin containing dithioaniline and thioaniline formed.

The preparation of resins by the action of sulphur chloride on primary aromatic amines was investigated by Meigs<sup>78</sup> who noted that higher temperatures tended to produce substances soluble in hydrocarbon solvents and to some extent in alcohol, whereas reaction at lower temperatures generally yielded masses having greater solubility in water. Products ranged from a pasty mass, part of which dissolved in oils and the rest in alcohol, to a resin (prepared with larger proportions of sulphur chloride) 60 per cent of which was insoluble in acids.

A secondary amine (diphenylamine) was treated by Ingram<sup>79</sup> with sulphur dichloride at 10°C. in carbon tetrachloride. The reaction was believed to proceed as follows:



The compound obtained was employed as an anti-oxidant in rubber mixes. Other secondary amines,<sup>80</sup> aniline<sup>81</sup> and amides<sup>82</sup> have been reported as giving a similar reaction with sulphur dichloride. Holzmänn<sup>83</sup> and Kym,<sup>84</sup> however, postulated formulas for the products obtained from diphenylamine and di- $\beta$ -naphthylamine in which hydrogen was removed from the ring. The structure of the compound from diphenylamine was represented by



Considering tertiary amines, apparently the only reaction possible is the removal of nuclear hydrogen, forming such compounds as bis(dimethylaminophenyl) sulphide<sup>85</sup> and disulphide.<sup>86</sup>

<sup>75</sup> S. Coffey, *Rec. trav. chim.*, 1921, 40, 747; *Chem. Abs.*, 1922, 16, 1225.

<sup>76</sup> T. Whittelsey and C. E. Bradley, U. S. P. 1,559,393, Oct. 27, 1925, to Naugatuck Chem. Co.; *Chem. Abs.*, 1926, 20, 126.

<sup>77</sup> V. Merz and E. Schmidt, *Ber.*, 1876, 9, 1050. E. B. Schmidt, *ibid.*, 1878, 11, 1168; *J.C.S.*, 1878, 34, 974.

<sup>78</sup> J. V. Meigs, U. S. P. 1,631,280, June 7, 1927, to Carleton Ellis; *Chem. Abs.*, 1927, 21, 2478.

<sup>79</sup> J. R. Ingram, U. S. P. 1,896,544, Feb. 7, 1933, to Rubber Service Laboratories Co.; *Chem. Abs.*, 1933, 27, 2845. Cf. E. I. Orlov, *Z. Farben-Ind.*, 1928, 20, 121; *Chem. Abs.*, 1928, 22, 2929.

<sup>80</sup> A. Michaelis and K. Luxembourg, *Ber.*, 1895, 28, 165; *J.C.S.*, 1895, 68 (1), 200.

<sup>81</sup> J. A. R. Smit, *Ber.*, 1875, 8, 1442; *Chem. Zentr.*, 1875, 805.

<sup>82</sup> K. G. Nauk, *J.C.S.*, 1921, 119, 1166.

<sup>83</sup> E. Holzmänn, *Ber.*, 1887, 20, 1640; 1888, 21, 2056; *J.C.S.*, 1887, 52, 723; 1888, 54, 1080.

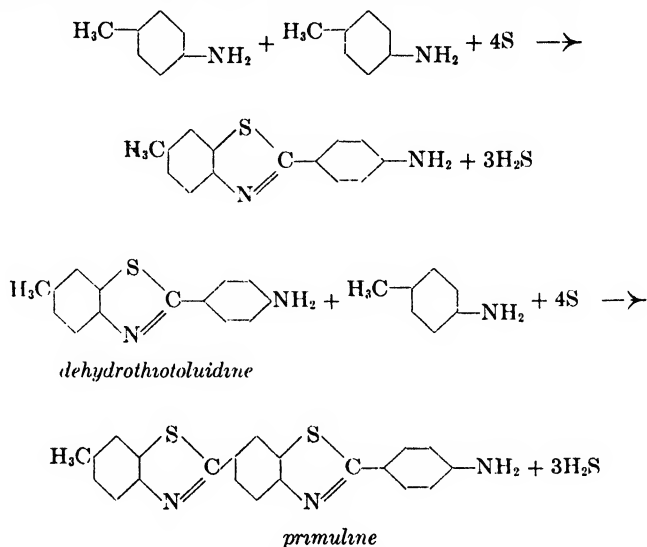
<sup>84</sup> O. Kym, *Ber.*, 1888, 21, 2807; 1890, 23, 2453; *J.C.S.*, 1889, 56, 51; 1890, 58, 1306.

<sup>85</sup> E. Holzmänn, *loc. cit.*

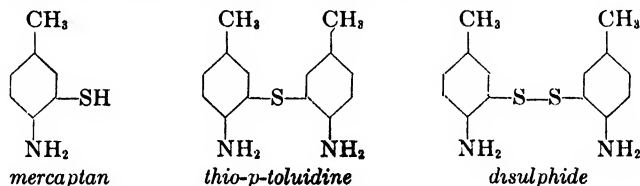
<sup>86</sup> Hannimann, *Ber.*, 1876, 10, 43; *Chem. Zentr.*, 1877, 310.



phide is liberated and two substances are isolated.<sup>80</sup> One is dehydrothiitoluidine (or p-aminophenyltoluthiazol) and the second is called Primuline.



The latter is a dye and, since it is insoluble, is used in the form of a sulphonated derivative. In all probability the molecule is larger than the formula indicates and is formed by a number of such condensations. Bogert and his co-workers<sup>80</sup> studied the reaction of p-toluidine and sulphur at lower temperatures (140-145°C.) in the presence of litharge. They postulate the initial reaction to be the formation of a mercaptan which is converted by the simultaneous oxidizing action of sulphur and litharge to thio-p-toluidine and a disulphide.



The disulphide formed in this reaction and that obtained from aniline have been found to improve the strength of cured rubber.<sup>81</sup> Resin formation has been reported to result on fusing the pure benzal derivative of o-amino-m-cresol (3-hydroxy-6-benzalaminotoluene) with sulphur.<sup>82</sup>

The previously mentioned researches on amines and sulphur apparently have not had as an objective the preparation of resins for molding or other commercial purposes, although resinous by-products are mentioned several times. Blumfeldt and Kaegi<sup>83</sup> found that brownish resins could be obtained by the action of

<sup>80</sup> A. Wahl, "The Manufacture of Organic Dyestuffs," transl. by F. W. Atack, G. Bell & Sons, London, 1914, 299. Cf. T. G. Levi, *Atti Congr. Naz. Chim. Ind.*, 1924, 400; *J.C.S.*, 1925, 128 (1), 440. R. F. Hunter, *J.S.C.I.*, 1923, 42, 302T.

<sup>81</sup> M. T. Bogert and M. R. Mandelbaum, *J.A.C.S.*, 1923, 45, 3045. M. T. Bogert and L. Smidth, *ibid.*, 1925, 50, 428.

<sup>82</sup> T. Kimishima, *Mem. Coll. Eng. Kyushu Imp. Univ. (Japan)*, 1927, 4, 193; *Chem. Abs.*, 1928, 22, 1496.

<sup>83</sup> M. T. Bogert and G. H. Connitt, *J.A.C.S.*, 1929, 51, 904.

<sup>84</sup> A. Blumfeldt and H. Kaegi, U. S. P. 1,654,856, Jan. 3, 1928, to Soc. anon. pour l'ind. chim à Bâle; *Chem. Abs.*, 1928, 22, 1051. British P. 214,242, 1923; *Chem. Abs.*, 1924, 18, 2612. German P. 401,168, 1923; *J.S.C.I.*, 1925, 44, 216B.

sulphur on primary and secondary amines with the exceptions of p-toluidine and N-alkylanilines. A transparent, yellowish-brown resin remains after heating 93 parts of aniline and 96 parts of sulphur, first at 185°C. and then for 21 hours at 250°C. The product softened above 100°C. and became insoluble and infusible when heated for a longer period.

Bly<sup>94</sup> reported that nickel, iodine and tungstic acid accelerated the interaction of sulphur and aniline at the latter's boiling point. Molded products fabricated from these resins were said to be good electrical insulators and to have smooth glossy surfaces. Aside from moldings, such products have been employed in anti-corrosive paints<sup>95</sup> and as binding agents in attaching abrasives to rubber.<sup>96</sup>

As with phenol-sulphur resins, several investigators have studied the modification of sulphur-amine compositions with formaldehyde. Application to the mounting of microscopic objects has been suggested for a condensation product of sulphur, aniline and formaldehyde.<sup>97</sup> Bedford<sup>98</sup> synthesized rubber-vulcanization accelerators by heating sulphur with an amine-formaldehyde condensate. Methylene diphenylamine (N,N'-diphenyl methylenediamine), anhydroformaldehydeaniline<sup>99</sup> and hexamethylenetetramine could be used.

**Miscellaneous Amine-Sulphur Resins.** Carbon disulphide was found by Lommel, Goost and Friedrich<sup>100</sup> to react with secondary alicyclic bases giving products of an oily or resinous nature which could be used in rubber vulcanizing. These were soluble with difficulty in ether or benzene, but some dissolved in chloroform, alcohol or water. For example, 76 parts of carbon disulphide were run gradually into a stirred and cooled mixture of 127 parts of hexahydroethyl-aniline, 99 parts of hexahydroaniline and 400 parts of ice water. The oily product (the hexahydroaniline salt of ethylhexahydrophenyldithiocarbamic acid) crystallized after some time. Carbon disulphide, primary amines (aniline, methyl- or butylamine) and aldehydes (butylaldehyde or acetaldehyde) also condense to form vulcanization accelerators.<sup>101</sup> The ratios of reactants were 2 mols of aldehyde, 1 or 2 mols of amine, and 1 mol of carbon disulphide.

Bigelow<sup>102</sup> studied the reaction taking place between benzalaniline and carbon disulphide in an autoclave at 170°C. The pure products isolated from the resulting tar were phenyl mustard oil, stilbene, thiobenzanilide and tetraphenylthiophene. Claus and Krall<sup>103</sup> found that the carbon disulphide which they used as a diluent for the reaction of sulphur chloride and aniline entered into the composition. The initial products were aniline hydrochloride, sulphur and thiocarbanilide. The last then reacted with the sulphur chloride to give triphenylguanidine and phenyl mustard oil. Carbon disulphide combines, as is well known, with alkali cellulose to form viscose. Harrison<sup>104</sup> reported that, when viscose is dissolved in water with an amine and oxidized, stable products are obtained which can be employed in making films and threads.

On refluxing sulphur with nitrobenzene, sulphur dioxide is given off and the mixture gradually thickens. Depending on the proportion of sulphur and length

<sup>94</sup> R. S. Bly, U. S. P. 1,761,291, June 3, 1930, to Cutler-Hammer, Inc.; *Chem. Abs.*, 1930, 24, 3662

<sup>95</sup> German P. 397,824, 1923, to C. F. Beer Sohne; *J.S.C.I.*, 1924, 43, 879B.

<sup>96</sup> British P. 389,238, 1933, to Azo A.-G.; *Chem. Abs.*, 1933, 27, 6021.

<sup>97</sup> *Science*, 1927, 65, 42. Cf. G. D. Hanna, *J. Roy. Microscopical Soc.*, 1931, 50, 424, *Chem. Abs.*, 1931, 25, 1858. See also Chapter 33.

<sup>98</sup> C. W. Bedford, U. S. P. 1,510,074, Sept. 30, 1924, to Goodyear Tire & Rubber Co.; *Chem. Abs.*, 1924, 18, 3740.

<sup>99</sup> See Chapter 33.

<sup>100</sup> W. Lommel, T. Goost and H. Friedrich, U. S. P. 1,863,572, June 21, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4346. Canadian P. 284,056, 1928; *Chem. Abs.*, 1929, 23, 608

<sup>101</sup> British P. 276,485, 1926, to E. I. du Pont de Nemours & Co.; *Brit. Chem. Abs. B*, 1927, 824.

<sup>102</sup> L. A. Bigelow, *J.A.C.S.*, 1923, 47, 183.

<sup>103</sup> A. Claus and W. Krall, *Ber.*, 1871, 4, 99; *J.C.S.*, 1871, 24, 364.

<sup>104</sup> W. Harrison, U. S. P. 1,684,732, Sept. 18, 1928; *Chem. Abs.*, 1928, 22, 4536.

of heating, Wilson<sup>106</sup> obtained resins of differing softening points. The mass formed by heating 369 parts of nitrobenzene and 160 parts of sulphur for 5-7 hours was mixed with fillers and cold molded. A stronger resin could be made by adding furfural to the mass before shaping the product. In this case the excess nitrobenzene was driven off first. The same was true of the hot-molding compositions made with higher proportions of sulphur.

A number of other products more or less related to the preceding ones have been reported. Thus, Binapfl and Strohmenger<sup>106</sup> prepared a vat dye by heating at 210°C. a mixture of azobenzene, o-cresol, sulphur and zinc chloride. Ishikawa<sup>107</sup> in studying the reaction of sulphur chloride on thioamides obtained  $\alpha$ -naphthimino- $\alpha$ -isothionaphthamide as a resinous substance. At 200°C., nitrobenzene, o,o'-dithioaniline and litharge react to form a black tar.<sup>108</sup> Matzurevich<sup>109</sup> refluxed aniline with thiosemicarbazide and hydrazinedithiocarboxamide and stated that in every case resinous by-products were formed. Thionylaniline condenses with malonic acid to form a resin.<sup>110</sup> As an anti-oxidant in rubber compositions, Scott<sup>111</sup> used a hard black resin made by heating an acetone- $\alpha$ -naphthil (obtained from acetone and  $\alpha$ -naphthylamine in the presence of iodine) with sulphur.

<sup>106</sup> W. C. Wilson, U. S. P. 1,732,453, Oct. 22, 1929, to Cutler-Hammer, Inc.; *Chem. Abs.*, 1930, 24, 253.

<sup>106</sup> J. Binapfl and L. Strohmenger, German P. 427,970, 1923, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1926, 781.

<sup>107</sup> S. Ishikawa, *Sci. Papers Inst. Phys. Chem. Research*, 1925, 3, 147; *Chem. Abs.*, 1925, 19, 3087.

<sup>108</sup> H. H. Hodgson, *J. Soc. Dyers and Col.*, 1925, 41, 99; *J. C. S.*, 1925, 128 (1), 506.

<sup>109</sup> I. Matzurevich, *Bull. soc. chim.*, 1927, 41, 637; *Chem. Abs.*, 1927, 21, 2901.

<sup>110</sup> P. Carre and D. Libermann, *Compt. rend.*, 1932, 194, 2218; *Chem. Abs.*, 1932, 26, 5925.

<sup>111</sup> W. Scott, U. S. P. 1,792,042, Feb. 10, 1931, to Rubber Service Lab. Co.; *Brit. Chem. Abs. B.*, 1931, 1063.

## Chapter 60

### Various Sulphur-Treated (Vulcanized) Products

Sulphur and sulphur halides react with a great variety of compounds. Aromatic amines, phenols,<sup>1</sup> fatty oils and various hydrocarbons all give sulphurized products. In certain cases, reaction occurs easily on simple mixing of the two reagents. This is true of the action of sulphur chloride on phenols, amines and unsaturated hydrocarbons.<sup>2</sup> However, when sulphur is employed, the temperature usually has to be raised before reaction takes place. Saturated hydrocarbons both of the aromatic and aliphatic series require the presence of a catalyst before any reaction with sulphur chloride starts.

The best-known vulcanizable hydrocarbon is rubber. Although a detailed description of the vulcanization of this substance is beyond the scope of the chapter, there are certain characteristics of hard rubber which relate it to synthetic resins. It is a good dielectric, and when mixed with softening agents and fillers it can be molded. It is also chemically resistant and, therefore, has been used both by itself and as a lining for steel in the manufacture of chemical apparatus. In the latter case, a layer of soft rubber is interposed between the hard rubber and the metal. Such an intervening layer makes the bond between the ebonite and the metal stronger and more elastic.<sup>3</sup> (See Figs. 164 and 165.)

#### REACTION OF SULPHUR COMPOUNDS WITH TERPENES

The primary action of sulphur on terpenes appears to consist in the formation of a monosulphide which then combines with more sulphur to form polysulphides.<sup>4</sup> A resin produced by the sulphurization of turpentine was obtained by Pratt<sup>5</sup> and is known as "Toron." This material was the result of work on a solvent (for reclaimed rubber) in which turpentine was the base. During the experimentation, sulphur was introduced and, on heating, it was observed that sulphur and turpentine formed a black viscous material. The hardness and viscosity of the resulting body depended on the time and temperature of the operation. Long heating at an elevated temperature gave a hard substance similar to mineral rubber. The product was readily soluble in benzene, toluene, xylene, gasoline and other hydrocarbon solvents and was partially soluble in acetone and alcohol. Solutions of Toron were thought to be non-colloidal since they penetrated the fibers of cloth

<sup>1</sup> See Chapter 59.

<sup>2</sup> See Chapter 54 for the discussion of the action of sulphur halides on rubber. In Chapter 10, various products are mentioned which are obtained from the reaction of sulphur and its halides on petroleum distillates. For a further discussion of the latter topic see Carleton Ellis, "Chemistry of Petroleum Derivatives," Chemical Catalog Co., Inc., New York, 1934.

<sup>3</sup> A review on hard rubber has been contributed by A. R. Kemp and R. S. Malon, *Ind. Eng. Chem.*, 1935, 27, 141. See also D. F. Twiss, *Trans. Inst. Rubber Ind.*, 1928, 3, 386; *Chem. Abs.*, 1928, 22, 2491. D. W. Kitchin, *Rubber Age (N. Y.)*, 1929, 24, 671; *Chem. Abs.*, 1929, 23, 2602. A. A. Perks, *J.S.C.I.*, 1926, 45, 142T. H. Dannenberg, *Kautschuk*, 1927, 104, 128; *Chem. Abs.*, 1927, 21, 3764. I. Minatani and I. Aoe, *J. Rubber Soc. Japan*, 1930, 2, 235; *Chem. Abs.*, 1931, 25, 4144.

<sup>4</sup> P. P. Budnikov and E. A. Schilow, *Ber.*, 1922, 55, 3848; *Chem. Abs.*, 1923, 17, 1005. Note also A. Nakatsuchi, *J.S.C.I. (Japan)*, 1930, 33, *Suppl. binding* 408; 1932, 35, *Suppl. binding* 376; 1933, 36, *Suppl. binding* 254; *Chem. Abs.*, 1931, 25, 938; 1932, 26, 5558; 1933, 27, 3927.

<sup>5</sup> W. B. Pratt, U. S. P. 1,349,909, Aug. 17, 1920; *Chem. Abs.*, 1920, 14, 3338. British P. 165,662, 1921. Cf. B. S. Rao, V. P. Shintre and J. L. Simonsen, *J.S.C.I.*, 1928, 47, 171T.

readily. Analyses and molecular-weight determinations indicated that sulphur had added to the olefinic linkages of the terpene and also that several terpene nuclei had been linked together. Since hydrogen sulphide was evolved it would further appear that some substitution had taken place.<sup>6</sup>

Toron is prepared by heating sulphur and turpentine together under a reflux condenser. At 150°C., the reaction progresses readily and the temperature is gradually raised to 200°C. The material can also be formed by digesting the two reactants together at 140°C.<sup>7</sup> The principal use for which Toron was intended was the impregnation of fabrics employed in the manufacture of rubber goods. Solutions of Toron, as was mentioned above, penetrate the fibers and facilitate the formation of a firm bond between the fabric and the rubber.<sup>8</sup> Cloth impregnated with solutions of these sulphur-terpene resins is reported to be waterproof.<sup>9</sup> Not only solutions of Toron but also aqueous emulsions can be used for such purposes.<sup>10</sup>

Gardner and Hart<sup>11</sup> prepared a similar material by heating turpentine and sulphur for about 12 hours at 120-130°C. Their product was used as a rubber accelerator and as an ingredient in a carbon-black pigment.<sup>12</sup>

Kobbe<sup>13</sup> heated 2 parts of pine oil with 1 part of sulphur at 190°C. for about 30 minutes. The resulting composition was then mixed at 120-140°C. with 25 parts of lubricating oil and the mixture employed as a cutting oil.<sup>14</sup> The reaction of various sulphurizing agents (sulphur, alkali sulphides and nitrogen sulphide) on pinene is stated by Budnikov<sup>15</sup> to produce a terpene sulphide of the formula,  $C_{10}H_{16}S$ . With gold chloride this sulphide formed a compound which could be used in gilding porcelain. Gray<sup>16</sup> thickened turpentine with sulphur chloride and utilized the product for bonding rubber to metal. Another material, an ingredient for rubber compositions, was obtained by blowing pine-tar oil with air at an elevated temperature and in the presence of a small proportion of sulphur.<sup>17</sup> Lubs, Fox and Smith<sup>18</sup> report that the action of sulphur chloride (75 g.) on pine oil (100 g.) at below room temperature (cooled with ice and then, after mixing, allowed to warm up to room temperature) followed by refluxing with alcoholic sodium sulphide (285 g. in 1000 cc.) produced an effective flotation agent. Other hydrocarbons and certain of their derivatives were also mentioned as forming similar products. Benzene and dichlorobenzene required catalysts before the reaction would take place. Aluminum chloride and aluminum amalgam were used for this purpose.

A number of varnishes have been made by heating sulphur with solutions of rubber. Such varnishes were used for impregnating fabrics to make them water-

<sup>6</sup> W. B. Pratt, *Ind. Eng. Chem.*, 1923, 15, 178.

<sup>7</sup> W. B. Pratt, U. S. P. 1,349,911, 1,349,912, 1,349,913 and 1,349,914, Aug. 17, 1920, to E. H. Clapp Rubber Co.; *Chem. Abs.*, 1920, 14, 3338. British P. 169,031, 169,513 and 169,514, 1920; *Chem. Abs.*, 1922, 16, 502, 856.

<sup>8</sup> Cf. J. B. Tuttle, *India Rubber World*, 1923, 67, 291; *Chem. Abs.*, 1923, 17, 1350.

<sup>9</sup> W. B. Pratt, U. S. P. 1,349,910, Aug. 17, 1920, to E. H. Clapp Rubber Co.; *J.S.C.I.*, 1921, 40, 154A. British P. 169,777, 1920, *Chem. Abs.*, 1922, 16, 802.

<sup>10</sup> W. B. Pratt, British P. 208,382, 1922; *Chem. Abs.*, 1924, 18, 1554.

<sup>11</sup> H. A. Gardner and L. P. Hart, U. S. P. 1,963,084, June 19, 1934, to Henry A. Gardner Laboratory, Inc.; *Chem. Abs.*, 1934, 28, 4939.

<sup>12</sup> H. A. Gardner, U. S. P. 1,963,896, June 19, 1934; *Chem. Abs.*, 1934, 28, 5261.

<sup>13</sup> W. H. Kobbe, U. S. P. 1,844,400, Feb. 9, 1932; *Chem. Abs.*, 1932, 26, 1892.

<sup>14</sup> Two other sulphur-containing cutting oils may be mentioned. W. H. Oldacre (U. S. P. 1,604,068, Oct. 19, 1926, to D. A. Stuart & Co.; *Chem. Abs.*, 1927, 21, 173) heated mineral oils with sulphur chloride at 80°C. O. E. Cushman and T. W. Doell (U. S. P. 1,806,933, May 26, 1931, to Standard Oil Co. of Calif.; *Chem. Abs.*, 1931, 25, 3954) caused sulphur to react with the unsaturated by-products of the Edleau process of oil refining.

<sup>15</sup> P. P. Budnikov, *Ber. deut. Keram. Ges.*, 1931, 12, 279; *Chem. Zentr.*, 1931, 2, 891. *Compt. rend.*, 1933, 196, 1898; *Chem. Abs.*, 1933, 27, 4789. See also L. Reschke, French P. 740,758, 1932; *Chem. Abs.*, 1933, 27, 2773.

<sup>16</sup> H. Gray, U. S. P. 1,697,275, Jan. 1, 1929, to B. F. Goodrich Co.; *Chem. Abs.*, 1929, 23, 1309.

<sup>17</sup> H. A. Winkelmann, U. S. P. 1,841,235, Jan. 12, 1932, to Philadelphia Rubber Works Co.; *Chem. Abs.*, 1932, 26, 1832.

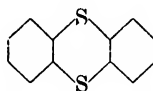
<sup>18</sup> H. A. Lubs, A. L. Fox and C. C. Smith, U. S. P. 1,875,062, Aug. 30, 1932, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1932, 26, 5897.



proof and electrically insulating.<sup>19</sup> As a solvent in this reaction, Pratt<sup>20</sup> employed turpentine which had previously been treated with oxalic acid. He states that the product was not a colloidal solution since it would pass through parchment. Another vulcanized terpene-rubber combination has been prepared by Gray<sup>21</sup> through heating 50 parts of pine oil, 100 parts of rubber, 80 parts of sulphur, 40 parts of clay and 2 parts of accelerator at 149°C. for 1 hour. When this composition was pulverized, it could be remolded at 177°C. in 2-5 minutes.

#### ACTION OF SULPHUR AND SULPHUR HALIDES ON AROMATIC HYDROCARBONS

The reaction of sulphur on benzene in the presence of a catalyst has been studied by Glass and Reid<sup>22</sup> and by Dougherty and Hammond.<sup>23</sup> The former investigators heated benzene and sulphur together in a bomb at 350°C. for 24 hours. The products isolated were thiophenol, diphenyl sulphide, diphenyl disulphide, thianthrene and hydrogen sulphide.



thianthrene

Dougherty and Hammond used aluminum chloride as catalyst and were able to isolate only thianthrene, diphenyl sulphide<sup>24</sup> and hydrogen sulphide. The mechanism suggested was:



Others have obtained thianthrene from benzene and sulphur chloride in the presence of metallic chlorides.<sup>25</sup> If the reaction is made to go further by using more sulphur chloride and by increasing the time and temperature, resinous substances are produced. Although the composition of these bodies is not known it is possible that they are in the form of chains containing sulphur-linkages similar to those present in thianthrene and diphenyl disulphide. Stegemann<sup>26</sup> observed that heating sulphur (1 per cent) with crude benzene at 250°C. for 2 hours formed a small amount of pitch, a reaction which Uloth<sup>27</sup> applied to the purification of benzene. Apparently the unsaturated compounds present in the crude distillate are the first to react and so are removed.

<sup>19</sup> British P. 243,966, 1925, to Mechanical Rubber Co.; *Chem. Abs.*, 1927, 21, 195. See also H. Plauson, British P. 326,216, 1928; *Brit. Chem. Abs.* B, 1930, 520.

<sup>20</sup> W. B. Pratt, U. S. P. 1,451,711, April 17, 1923; *Chem. Abs.*, 1923, 17, 2064.

<sup>21</sup> H. Gray, U. S. P. 1,769,506, July 1, 1930, to B. F. Goodrich Co.; *Chem. Abs.*, 1930, 24, 4666.

<sup>22</sup> H. B. Glass and E. E. Reid, *J. A.C.S.*, 1929, 51, 3428.

<sup>23</sup> G. Dougherty and P. D. Hammond, *J. A.C.S.*, 1935, 57, 117. See also J. Boeseken, *Rec. trav. chim.*, 1905, 24, 221; *J.C.S.*, 1905, 88 (1), 583.

<sup>24</sup> Diphenyl sulphide forms an amorphous perchlorate,  $\text{C}_6\text{H}_5\text{S}(\text{OClO}_2)=\text{C} < (\text{CH}=\text{CH})_2 \text{CH}_2$ . O. Hinsberg, *Ber.*, 1929, 62, 127; *Chem. Abs.*, 1929, 23, 2703.

<sup>25</sup> German P. 372,664, 1916, to Dubois & Kaufmann Chem. Fabr.; *J.S.C.I.*, 1923, 42, 1141A.

<sup>26</sup> W. Stegemann, *Z. angew. Chem.*, 1928, 41, 626.

<sup>27</sup> R. Uloth, *Brennstoff-Chem.* 1929, 10, 297; *Brit. Chem. Abs.* B, 1929, 767. F. Hofmann and R. Uloth, British P. 306,421, 1929; *Chem. Zentr.*, 1929, 2, 963.

Hassler<sup>28</sup> obtained tanning agents<sup>29</sup> and varnishes<sup>30</sup> by fusing naphthalene,<sup>31</sup> sulphuric acid and sulphur together at 160-180°C. In place of the naphthalene and sulphuric acid a naphthalenesulphonic acid<sup>32</sup> could be used. The products were bluish-black before neutralization of the acid, but afterwards they were yellowish brown. Some of these resins were water-soluble whereas those produced using more sulphur and less sulphuric acid were insoluble. Experiments in the author's laboratory have given more information as to these relationships. When the following proportions were employed the product was soluble in water and fusible:

Naphthalene . . . . .	50 parts
Sulphur . . . . .	15
Sulphuric acid . . . . .	125

Raising the sulphur to 24 parts and reducing the sulphuric acid to 60 yielded a material only part of which was water-soluble. The water-insoluble portion could be mixed with filler and hot molded to give an article having a hard glossy surface. Raising the sulphur to 36 parts resulted in an insoluble and infusible black solid.

Delaney and Richardson<sup>33</sup> heated equal parts of naphthalene and sulphur monochloride together in the presence of a catalyst, e.g., tin, aluminum or ferrous sulphides, and obtained a resin suggested for use in making phonograph records. The temperature was held at around 95°C. at which point the reaction goes rather rapidly. The product on hot molding became substantially insoluble and infusible. Cherry<sup>34</sup> reported that wear-resistant phonograph records can be made of a composition containing naphthalene-sulphur resin, ozokerite and an appropriate filler.

Anthracene and sulphur chloride yield 9-anthryl dithiochloride, ( $C_{14}H_9S_2Cl$ ), a yellowish-red crystalline compound melting at 117-118°C. and reacting with ammonia and aromatic bases to form resinous bodies.<sup>35</sup> It has also been observed that sodium disulphide reacts with dibromoanthracene, when heated in an autoclave, to form a yellow, insoluble and amorphous compound.<sup>36</sup> Frey<sup>37</sup> reported that anthracene (25 per cent) and sulphur (2.5 per cent) heated with coal-tar pitch resulted in a product similar in chemical and physical properties to the original pitch. Further, the sulphurized products made by heating cuprene<sup>38</sup> with benzene and sulphur or sulphur chloride have been stated to be of use in the rubber industry.<sup>39</sup>

A chemically resistant material has been obtained by Balle and Daimler<sup>40</sup> by incorporating a sulphurized aromatic hydrocarbon resin with a fusible phenol-formaldehyde condensation product. Thus, 400 parts of technical xylol were

<sup>28</sup> F. Hassler, U. S. P. 1,533,594, April 14, 1925; *Chem. Abs.*, 1925, 19, 1791. German P 407,994, 1918, and 409,713, 1920; *J.S.C.I.*, 1925, 44, 517B, 642B. German P 406,269, 1926, *Chem. Abs.*, 1929, 23, 2257.

<sup>29</sup> Using sulphur chloride in a similar reaction between naphthalene and sulphuric acid, a resist for use in dyeing animal fibers has been obtained (Faibw vom Meister, Lucius & Bruning, British P 248,007, 1926, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.*, 1927, 628). See Chapter 59 for some other resists made from sulphur chloride and phenols.

<sup>30</sup> Sulphuric acid is reported as being a catalyst for the preparation of varnishes from naphthalene and sulphur chloride (A. Ya. Savitzkii and P. G. Novak, Russian P. 33,299, 1933; *Chem. Abs.*, 1934, 28, 3605).

<sup>31</sup> The material known as "Hyrax" and which is used in mounting microscopic objects is said to be a naphthalene resin (G. D. Hanna, *J. Roy. Microscopical Soc.*, 1931, 50, 424; *Chem. Abs.*, 1931, 25, 1858).

<sup>32</sup> J. L. Heid (*J.A.C.S.*, 1927, 49, 844) has reported that tars are obtained by heating naphthalene-2,7-disulphonic acid at 180°C.

<sup>33</sup> M. E. Delaney and L. T. Richardson, U. S. P. 1,655,942, Jan. 10, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 105.

<sup>34</sup> O. A. Cherry, U. S. P. 1,671,228, May 29, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 2644.

<sup>35</sup> P. Friedländer and A. Simon, *Ber.*, 1922, 55, 3969; *J.C.S.*, 1923, 124 (1), 109.

<sup>36</sup> W. H. Cooke, I. M. Heilbron and G. H. Walker, *J.C.S.*, 1925, 127, 2250.

<sup>37</sup> K. Frey, *Asphalt u. Teer*, 1932, 33, 26, *Brit. Chem. Abs.*, B, 1933, 903.

<sup>38</sup> See Chapter 8.

<sup>39</sup> German P. 406,147, 1922, to Elektrizitätswerk Lonza; *J.S.C.I.*, 1925, 44, 379B.

<sup>40</sup> G. Balle and K. Daimler, German P. 475,478, 1922, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 3360. See also German P. 471,835, 1924, addn. to 455,551, 1923, to Sinit A.-G.; *Chem. Abs.*, 1929, 23, 2540.

reacted with 500 parts of sulphur monochloride and 8 parts of zinc chloride. One hundred parts of the resulting resin were fused with 30-50 parts of a condensation product from cresol and formaldehyde. The mixture was a black mass possessing a high melting point.

#### VULCANIZED BITUMINOUS MATERIALS

Numerous investigators have suggested that useful materials can be prepared by the action of sulphur or sulphur chloride on bituminous substances. Since in most, if not all, of these cases the initial substance is a complex mixture, very little can be said about the structures of the resulting products. However, the principal reaction is probably with any unsaturates present, since Lorand<sup>41</sup> has shown that it is the olefinic constituents of petroleum distillates which interact primarily with sulphur chloride. The saturated hydrocarbons were found to react much more slowly giving chlorinated (not sulphurized) materials. Two suggested applications for the bodies obtained by treating tar oils with sulphur and sulphur chloride are the preparation of black printing colors<sup>42</sup> and ingredients for paints.<sup>43</sup> Hessele<sup>44</sup> obtained sulphurized products by heating a hydrocarbon oil with sulphur in the presence of catalysts such as the oxides and hydroxides of chromium, manganese, iron, cobalt and nickel. Hessele also stated that resinous and heavy polymerized masses resulted when the metallic catalyst was omitted.

Kurath<sup>45</sup> described the use of stearin pitch in a cold-molding composition prepared by melting together 1050 parts of stearin pitch, 945 parts of coal-tar pitch and 105 parts of gilsonite at 260°C. The mixture was cooled to 246°C. and 168 parts of fish oil were added. An emulsion of 40 parts of this binder and 9 parts of sulphur in 6 parts of water was then added to 150 parts of asbestos. The resulting mass was disintegrated and molded. Pungs<sup>46</sup> heated stearin pitch with sulphur, wood oil, whale oil and an extract of tar and obtained an adhesive and impregnating composition to be used in treating textiles. A related body formed by vulcanizing a mixture of linseed oil and stearin pitch has been employed as an insulating compound.<sup>47</sup>

Asphalt and similar bituminous materials have been heated with sulphur to make a vulcanized impregnant for stone,<sup>48</sup> a briquet binder<sup>49</sup> and a product for use in road-making.<sup>50</sup> Bolgar<sup>51</sup> heated asphalt and sulphuric acid together until the mixture was homogeneous, allowed the mass to cool and then stirred in sand. In this way he obtained a plastic composition. Sulphonation of sulphurized coal-tar is said to produce a tanning agent.<sup>52</sup>

As was noted previously, benzene is relatively inert to sulphur. An anti-corrosive paint has been prepared by mixing in a benzene vehicle asphalt, rubber and gum elemi, followed by heating with sulphur, sulphur chloride or arsenic sulphide.<sup>53</sup>

<sup>41</sup> E. Lorand, *Ind. Eng. Chem.*, 1927, 19, 733.

<sup>42</sup> German P. 364,830, 1920, to Rutgerswerke A.-G.; *J.S.C.I.*, 1923, 42, 614A.

<sup>43</sup> German P. 577,116, 1933, to Lackfabrik Ewald Dorken; *Chem. Abs.*, 1933, 27, 4107.

<sup>44</sup> E. T. Hessele, U. S. P. 1,996,334, Apr. 2, 1935, to Thiophene Products Co.

<sup>45</sup> F. Kurath, U. S. P. 1,732,478, Oct. 22, 1929, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1930, 24, 212.

<sup>46</sup> W. Pungs, U. S. P. 1,916,584, July 4, 1933, to I. G. Farben und A.-G.; *Chem. Abs.*, 1933, 27, 4693. Canadian P. 282,877, 1928; *Chem. Abs.*, 1928, 22, 4214. British P. 302,710, 1927; *Chem. Abs.*, 1929, 23, 4308. French P. 644,965, 1927; *Chem. Abs.*, 1929, 23, 2000.

<sup>47</sup> L. Bärnhielm and A. Jernander, British P. 3,045, 1894; *J.S.C.I.*, 1894, 13, 531.

<sup>48</sup> L. Cohen, British P. 271,722, 1926; *Chem. Abs.*, 1928, 22, 1665.

<sup>49</sup> R. E. Willard, U. S. P. 1,869,083, July 26, 1932, to Briquet Engineering Co.; *Chem. Abs.*, 1932, 26, 5404.

<sup>50</sup> A. F. Campbell, British P. 239,264, 1924, to Hardman and Holden, Ltd.; *J.S.C.I.*, 1925, 44, 883B. In this case the sulphur is driven off as hydrogen sulphide.

<sup>51</sup> L. Bolgar, Swiss P. 129,309, 1927; *Chem. Abs.*, 1929, 23, 3793.

<sup>52</sup> W. Moeller, British P. 193,722, 1922; *J.S.C.I.*, 1923, 42, 367A.

<sup>53</sup> C. H. Iverson and G. S. Roberts, British P. 161,201, 1919; *J.S.C.I.*, 1921, 40, 399A.

Titzel<sup>54</sup> mixed gilsonite, vulcanized rubber, manganated linseed oil, turpentine, petroleum naphtha and sulphur. The solution was applied to surfaces and baked like a japan.

Castor oil and petroleum pitch have been vulcanized together with sulphur to make an impregnating agent.<sup>55</sup> Alley<sup>56</sup> used a mixture of raw linseed oil, bituminous coal, asbestos and sulphur in making a friction material for brakes. Rubber and gutta-percha substitutes have been prepared by melting together pitch, tung oil and sulphur chloride. Free sulphur was added to the fused mass.<sup>57</sup> In case a more rubbery product was desired a certain amount of rubber itself could be added, whereas the addition of paraffin wax furnished a product more like gutta-percha.

Attempts to improve the residues from the refining of petroleum,<sup>58</sup> anthracene,<sup>59</sup> oils,<sup>60</sup> fats<sup>61</sup> and fatty acids<sup>62</sup> include heating them with sulphur chloride or sulphur. Wood may be reconditioned by filling abraded spike holes and similar im-

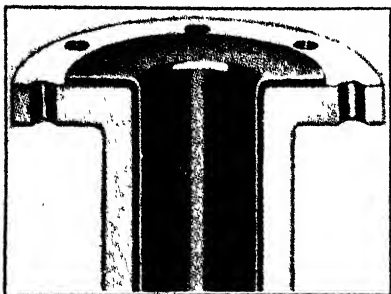


FIG. 164.

Hard-Rubber Lining Bonded to Metal Pipe.

Courtesy American Hard Rubber Company

perfections with a vulcanized composition of rubber, castor oil and sulphurized asphalt.<sup>63</sup> Vulcanized rubber dissolved in a mixture of water-gas tar and coke-oven tar and heated with sulphur gave a product which could be used in electrical insulation and in road building.<sup>64</sup>

Reif<sup>65</sup> developed a procedure for making plastic compositions from fibrous materials and sulphurized tars. The loose fibers were saturated with ammonia or dusted with a powdered base (calcium hydroxide or sodium carbonate) and then sprayed with tar. Each fiber was thus coated with a thin layer which was then vulcanized by a spray of sulphur chloride. The hydrogen chloride liberated from the reaction was neutralized by the base present. The final product could be molded when hot.

<sup>54</sup> J. A. Titzel, U. S. P. 391,927, Oct. 30, 1888.

<sup>55</sup> British P. 239,500, 1925, to Norsk Hydro-Elektrisk Kvaestofaktieselskab.; *Brit. Chem. Abs.* B, 1926, 501. See also C. Hørbye, Canadian P. 260,711, 1926; *Chem. Abs.*, 1926, 20, 3564.

<sup>56</sup> J. D. Alley, U. S. P. 1,882,702, Oct. 18, 1932, to American Brake Materials Corp.; *Chem. Abs.*, 1933, 27, 820. German P. 583,464, 1933; *Chem. Abs.*, 1934, 28, 272

<sup>57</sup> *Kunststoffe*, 1925, 15, 56

<sup>58</sup> G. A. Le Roy, *Bull. Soc. Ind. Mulhouse*, 1907, 77, 147; *J.S.C.I.*, 1907, 26, 754.

<sup>59</sup> German P. 332,888, 1919, addn. to 330,970, 1919, to Verkaufsverein. f. Teererzeugnisse G.m.b.H.; *J.S.C.I.*, 1921, 40, 427A.

<sup>60</sup> G. Balle, German P. 410,012, 1923, to Farb. vorm. Meister, Lucius & Brüning; *J.S.C.I.*, 1925, 44, 493B.

<sup>61</sup> M. Melamid, German P. 386,062, 1921, addn. to 335,323, 1919; *J.S.C.I.*, 1924, 43, 302B. See also German P. 434,143, 1923; *Brit. Chem. Abs.* B, 1927, 495. W. Griscorn, Jr., U. S. P. 529,905, Nov. 27, 1894, to Standard Paint Co. British P. 22,966, 1894; *J.S.C.I.*, 1895, 14, 285.

<sup>62</sup> W. Savage, U. S. P. 1,669,490 and 1,669,491, May 15, 1923, to Savage-Rubber Corp.; *Chem. Abs.*, 1928, 22, 2494.

<sup>63</sup> S. Krishna, British P. 382,557, 1932; *Brit. Chem. Abs.* B, 1933, 21.

<sup>64</sup> E. O. Rhodes and F. D. Hager, U. S. P. 1,884,240, Oct. 25, 1932, to Amer. Tar Products Co.; *Chem. Abs.*, 1933, 27, 1067.

<sup>65</sup> N. Reif, U. S. P. 895,197, Aug. 4, 1908; *Chem. Abs.*, 1908, 2, 3290. German P. 332,941, 1920; *J.S.C.I.*, 1921, 40, 427A.

## SULPHURIZATION OF NATURAL AND SYNTHETIC RESINS

When rosin, abietic acid, abietene or abietane is heated with sulphur and then distilled, retene is obtained.<sup>66</sup> Under milder treatment than distillation, less thorough changes in the molecule take place and various sulphurized bodies have been obtained. Thus, Moltke-Huitfeldt<sup>67</sup> heated rosin (500 g.) and sulphur (125 g.) for 1 hour at 155-160°C. The powdered mass after cooling was dissolved in sodium carbonate solution at 100°C. A transparent, yellow, gelatinous soap was obtained. Valenta<sup>68</sup> added sulphur to melted rosin and secured a black product closely resembling Syrian asphalt in properties. It did not dissolve in alcohol but was soluble in benzene and chloroform. On evaporation, a benzene solution left a solid film which became insoluble when exposed to light.

Rosin and a number of other natural resins are too soft to make good varnishes.<sup>69</sup> Low<sup>70</sup> reports that they can be hardened by heating under pressure with an aqueous suspension of sulphur. Prager<sup>71</sup> states that the addition of 5-10 per cent of sulphur at 140-150°C. produces a dark green, stable material. Various non-metallic inorganic sulphur compounds (sulphur chloride, chlorosulphonic acid, sulphuric acid and thionyl chloride) have been used also to modify rosin.<sup>72</sup>

Nielsen<sup>73</sup> heated 50 parts of rosin with 25 parts of mineral oil ("medium" automobile oil) to 102°C. A thin stream of melted sulphur (at 123°C.) was poured in with agitation. When cold, 10 parts of rice flour were incorporated and the product was suggested as a mastic composition in laying wood blocks. An artificial gutta-percha has been prepared by Zingler<sup>74</sup> from a mixture of copal, sulphur flowers and petroleum or turpentine. After cooling, the mass was mixed with an ammoniacal solution of casein and heated to 126-150°C. until it had the consistency of a thin fluid. It was then boiled with 15-25 per cent of tannic acid and finally washed with water and dried.

Ohta<sup>75</sup> made an electrical insulating varnish by heating tung oil and rosin with sodium sulphide or selenide. Aluminum was used as a catalyst and the temperature was held between 240° and 300°C. Selenium (0.1 per cent) added to a mixture of a drying oil and a natural resin is said to prevent the mixture from burning during the heating required to produce a varnish.<sup>76</sup> Papier-mâché or wood has been impregnated with a composition made from resin, lime, boiled linseed oil and sulphur. This product, according to Faure,<sup>77</sup> is acid-proof and applicable for making storage batteries. A fiberboard has been made by coagulating a suspension of fibers, sulphur and rosin size with alum followed by forming into sheets.<sup>78</sup>

Urushiol is one of the principal constituents of the juice obtained from the Japanese varnish tree, *Rhus vernicifera*.<sup>79</sup> This juice (Japanese lacquer) is poisonous to the skin but, according to Satow,<sup>80</sup> is rendered nonpoisonous when

<sup>66</sup> German P. 43,802, 1887, to A.-G. f. chem. Ind.; *Chem. Zentr.*, 1888, 1372. T. H. Easterfield and G. Bagley, *J.C.S.*, 1904, 85, 1247. A. Vesterberg, *Ber.*, 1903, 36, 4200; *J.C.S.*, 1904, 86 (1), 151. W. Schultze, *Ann.*, 1908, 359, 131, 138; *J.C.S.*, 1908, 94 (1), 356.

<sup>67</sup> L. de Moltke-Huitfeldt, French P. 629,214, 1927; *Brit. Chem. Abs.* B, 1929, 254.

<sup>68</sup> E. Valenta, *Central-Org. f. Warenkunde u. Technol.*, 1891, 1, 19; *Chem. Zentr.*, 1891, 2, 687.

<sup>69</sup> See Chapter 37.

<sup>70</sup> F. S. Low, U. S. P. 1,243,312, Oct. 16, 1917; *Chem. Abs.*, 1918, 12, 233.

<sup>71</sup> O. Prager, *Seifensieder-Ztg.*, 1915, 42, 705; *Chem. Abs.*, 1915, 9, 3369.

<sup>72</sup> L. Auer, *British P.* 237,750, 1929; *Chem. Abs.*, 1931, 25, 2312.

<sup>73</sup> H. C. Nielsen, U. S. P. 1,841,067, Jan. 19, 1932, to National Wood Products Co.; *Chem. Abs.*, 1932, 26, 1811.

<sup>74</sup> M. Zingler, German P. 20,939, 1882; *J.S.C.I.*, 1883, 2, 287.

<sup>75</sup> H. Ohta, U. S. P. 1,801,364, April 21, 1931, to Asaki Garasu K. K.; *Chem. Abs.*, 1931, 25, 3502.

<sup>76</sup> French P. 638,197, 1927; *Chem. Abs.*, 1929, 23, 293. *British P.* 301,341, 1927; *Chem. Abs.*, 1929, 23, 4089.

<sup>77</sup> Y. Inada, Japanese P. 100,206, 1933, to Tokyo E. C. Kogyo K. K.; *Chem. Abs.*, 1934, 28, 2554.

<sup>78</sup> C. A. Faure, U. S. P. 366,717, July 19, 1887, to Electrical Accumulator Co.

<sup>79</sup> J. Carnie, U. S. P. 1,843,943, Feb. 9, 1932, to Mechanical Rubber Co.; *Chem. Abs.*, 1932, 26, 2057.

<sup>80</sup> See Chapter 2.

<sup>81</sup> T. Satow, U. S. P. 1,754,243, April 15, 1930; *Chem. Abs.*, 1930, 24, 2903.

heated with 40-60 parts of sulphur at 120-160°C. The product was converted by treatment with formaldehyde or acetaldehyde to a rapidly hardening material, which could be mixed with fillers and molded or used as an impregnating or coating agent when dissolved in benzene, benzene or acetone. The coatings were insulators for electricity. They could also be utilized as glues in veneering. A similar protective layer has been made by pasting a sheet of asbestos paper to a surface, followed by painting with vulcanized urushiol and heating to 150-200°C. This layer was said to be resistant to hydrochloric and other acids.<sup>81</sup> A mixture of vulcanized Japanese lacquer, hard rubber and a polymerized mixture of a drying oil and manganese or cobalt resinate have also provided an electrical insulation.<sup>82</sup>

Venugopalan<sup>83</sup> studied the effect of sulphur and sulphur chloride on shellac. He reports that the mechanical properties and water resistance of the varnishes and molded products made from vulcanized shellac were both improved. Treatment with sulphur was carried out by heating the shellac with 3-4 per cent of sulphur at 180°C. until the product after cooling was green in color. When sulphur chloride is added in chloroform solution to a varnish made of shellac, it is stated that not only is the water resistance increased, but also the color is improved. These changes, according to Aldis,<sup>84</sup> are due to the hydrochloric acid liberated.

Resin-like substances have been obtained by treating salts of resinic, humic or lignoceric acids with chlorides of aromatic sulphonic acids.<sup>85</sup> For example, 100 kg. of  $\alpha$ - or  $\beta$ -naphthalenesulphonyl chloride were added to a solution of 120 kg. of sodium colophionate in 100-200 kg. of water. The solution was heated at 30°C. for 12 hours and then allowed to cool. The precipitate formed (separated by decantation or filtration) was then dissolved in benzene for the purpose of purification. The organic acid salts could be replaced by soft coal-tar pitch or anthracene-oil distillates. The products were used as varnishes.

A number of synthetic resins<sup>86</sup> have been vulcanized. Arsem<sup>87</sup> heated the reaction product of glycerol, phthalic anhydride and oleic acid with 10-30 per cent of sulphur. The product was an elastic rubber-like material. Ellis<sup>88</sup> treated solutions of alkyd resins with sulphur chloride. He found that a restricted amount of the halide (1-2 per cent) was desirable since otherwise the product was darker in color. For example, a resin was prepared from 80 parts of phthalic anhydride, 50 parts of glycerol and 40 parts of distilled cottonseed fatty acids. One thousand parts of this resin were then dissolved in 1500 parts of a mixture of benzene and ethyl acetate (equal parts). To the solution were added 10 parts of sulphur monochloride, the mixture stirred thoroughly and allowed to stand for 2 hours. Magnesium oxide (5 parts) was incorporated to neutralize the acid and the solution was filtered. Such a resin solution gave coatings which were less tacky than those formed using the unvulcanized alkyd. On heating, the films became substantially infusible and insoluble. Nitrocellulose could be added to these compositions. Resins to be used in varnishes have also been obtained by Ott, Steinmeyer and Frick<sup>89</sup>

<sup>81</sup> K. Ikeda, Japanese P. 95,559, 1932; *Chem. Abs.*, 1933, 27, 3301.

<sup>82</sup> T. Mori, Japanese P. 100,994, 1933, to T. Sawafuji; *Chem. Abs.*, 1934, 28, 4038.

<sup>83</sup> M. Venugopalan, *Indian Lac Research Inst., Research Notes*, 1933, 10, 12; 1934, 18; *Chem. Abs.*, 1934, 28, 2202, 6336.

<sup>84</sup> R. W. Aldis, *Indian Lac Research Inst., Research Notes*, 1934, 18; *Brit. Chem. Abs.* B, 1935, 33.

<sup>85</sup> M. Melamid, British P. 133,712 and 133,713, 1919; *J.S.C.I.*, 1921, 40, 399A. Cf. the decomposition of benzyl and allyl benzenesulphonates to amorphous hydrocarbons, Z. Foldi, *Ber.*, 1927, 60, 656; *Brit. Chem. Abs.* A, 1927, 453.

<sup>86</sup> I. Kreidl (French P. 747,688, 1933; *Chem. Abs.*, 1933, 27, 5203) uses thiosulphates and polythionates as vulcanizing agents for synthetic resins, whereas sulphur itself is used in German P. 635,007, 1928, to Firma Ewald Dörken; *Chem. Abs.*, 1932, 26, 1144.

<sup>87</sup> W. C. Arsem, U. S. P. 1,082,106, Dec. 23, 1913, to Gen. Electric Co.; *Chem. Abs.*, 1914, 8, 830. British P. 9085, 1913, to Brit. Thomson-Houston Co., Ltd.; *J.S.C.I.*, 1913, 32, 1023. For a discussion of modified alkyd resins containing drying oil acids see Chapter 44.

<sup>88</sup> Carleton Ellis, U. S. P. 1,811,115, June 23, 1931; *Chem. Abs.*, 1931, 25, 5049.

<sup>89</sup> K. Ott, H. Steinmeyer and F. Frick, German P. 526,802, 1929, to I. G. Farbenind. A.-G.; *Chem.*

by vulcanizing alkyd resins (modified by drying oil acids) with less than 5 per cent of sulphur.

According to Herrmann and Haehnel,<sup>90</sup> polyvinyl alcohol and its derivatives give products resembling rubber when treated with sulphur or sulphur chloride. Thus, they heated polyvinyl alcohol at 150°C. for 5 hours with 1 per cent of sulphur. The resulting material was black, hard and rubber-like. It could be worked by cutting or sawing. The use of a 10 per cent solution of sulphur monochloride in carbon disulphide produced a plastic material resembling soft rubber.

Lender<sup>91</sup> states that coatings of polymerized cumarone and indene become fissured and brittle in time. This he reports is largely prevented if the resin is heated with sulphur or sulphur chloride before using it in a varnish. It has already been noted that the insolubility of phenol-formaldehyde resins in the final stage of condensation hindered their application to oil varnishes.<sup>92</sup> In one of the methods for avoiding this difficulty, a fusible phenolic resin is vulcanized at 332°C. with sulphur or with a sulphurized organic compound (turpentine or chlorinated biphenyl). Tung-oil solutions of the product can be bodied by heating to 315°C. without formation of insoluble complexes.<sup>93</sup>

#### VULCANIZED FATTY OILS AS COATINGS

The vulcanization of drying and non-drying fatty oils produces, first, viscous liquid compositions and, second, solid rubber-like bodies.<sup>94</sup> The former are used as coatings and it should be noted that the films from the treated oils are more waterproof and do not penetrate various porous materials. Also, the vulcanized drying oils are said to permit of a more rapid application of successive coats, a property which will be considered more fully later in the chapter in connection with the Frenkel process.

According to Whitby and Chataway,<sup>95</sup> linseed oil reacts with sulphur in three successive steps. The sulphur first combines chemically with the oil. This reaction is relatively rapid, 45 minutes at 160°C. being required for the combination of up to 16.5 per cent of sulphur. Following this, an acetone-insoluble polymer begins to accumulate. This substance is richer in sulphur than the remaining liquid. The mass becomes progressively more viscous and eventually sets to a gel. Concentrated sulphuric acid converts the thick acetone-insoluble oil instantly to a solid polymer, and a similar result is obtained by continuing the heating after the oil has set or by using a larger proportion of sulphur.

The material formed by the action of sulphur chloride on blown linseed oil has been employed by Frenkel and Brust<sup>96</sup> to replace the colloiddally dispersed glass, kaolin or diatomaceous earth commonly used in priming coats. Thus, 30 parts of blown linseed oil were treated with 1-2 parts of sulphur chloride and 40 parts of linseed oil were added before the reaction was complete. Driers were then incorporated and the consistency was adjusted by thinning with ben-

<sup>90</sup> *Abs.*, 1931, 25, 4984. *British P.* 338,604, 1929; *Chem. Abs.*, 1931, 25, 2531. See also J. Scheiber, *German P.* 560,371, 1932, addn. to 543,287, 1930; *Chem. Abs.*, 1933, 27, 1220.

<sup>91</sup> W. O. Herrmann and W. Haehnel, *U. S. P.* 1,672,157, June 5, 1928, to Consort. f. elektrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1928, 22, 2686. See also *British P.* 294,474, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 2072. *French P.* 695,300, 1930, *Chem. Abs.*, 1931, 25, 2878. See also Chapters 51 and 52.

<sup>92</sup> R. Lender, *German P.* 277,605, 1913; *Chem. Abs.*, 1915, 9, 1127.

<sup>93</sup> See Chapter 19 for the preparation of oil-soluble phenolic resins.

<sup>94</sup> H. A. Gardner, *U. S. P.* 1,992,570, Feb. 26, 1935.

<sup>95</sup> See the section on factice below. A rubber substitute has also been obtained by vulcanising an alkaline extract of seaweed (C. A. Houques-Fourcade, *U. S. P.* 1,772,218, Aug. 5, 1930; *Chem. Abs.*, 1930, 24, 4906).

<sup>96</sup> G. S. Whitby and H. D. Chataway, *J.S.C.I.*, 1926, 45, 115T. See also J. S. Long, C. A. Knauss and J. G. Smull, *Ind. Eng. Chem.*, 1927, 19, 62.

<sup>97</sup> E. W. Frenkel and A. Brust, *U. S. P.* 1,936,230, Nov. 21, 1933, to Pittsburgh Plate Glass Co.; *Chem. Abs.*, 1934, 28, 917. *Austrian P.* 118,585, 1930, addn. to 115,309, 1929, to Firma H. Frenkel; *Chem. Zentr.*, 1930, 2, 4335.

zene.<sup>97</sup> A somewhat similar product has been prepared by Branscombe and Everleigh.<sup>98</sup>

Coatings produced by sulphurized oils are relatively impervious. Hollander<sup>99</sup> found that the sulphur treatment of linseed oil reduced its swelling tendency to a degree comparable with that of stand oil, and under certain conditions the water resistance of tung oil was reached. Rydberg<sup>100</sup> made leather impervious to water by soaking it in a drying oil and then treating with sulphur monochloride. The material obtained by the action of sulphur chloride on tung oil has been proposed by Atkins<sup>101</sup> as a protective coating to render concrete resistant to oil, water, and weather influences. Balloons have also been varnished with a preparation of oils and sulphur chloride.<sup>102</sup> Brandenberger and Riedemann<sup>103</sup> reported that a solution of an oil sulphurized with sulphur chloride was useful in making paints for ship bottoms. Further, this coating was stated to be a good rust preventive. However, Brendel<sup>104</sup> has disputed this, saying that such varnishes may even be corrosive due to the residual hydrochloric acid which they contain.

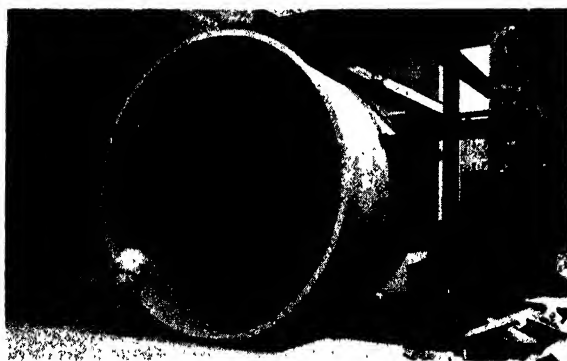


FIG. 165.  
Tank Lined with Hard Rubber.

Courtesy American Hard Rubber Company

Osnos and Golovistikov<sup>105</sup> studied the reaction of sulphur monochloride and linseed oil in the attempt to prepare varnishes involving the use of smaller quantities of halide. They found that the oxidized oil permitted the desired decrease in the amount of reagent and that the resulting varnish was better than those containing 14-16 per cent of sulphur monochloride. Heublyum<sup>106</sup> reviewed their work and also came to the conclusion that the amount of sulphur chloride should be kept as low as possible. Others who have investigated the use of sulphur- and sulphur chloride-treated oils have reported that a sulphur-treated tung oil has not only an increased alkali resistance, but also an increased tendency to blister on plaster.<sup>107</sup> The latter property is probably due to its impermeability to moisture. Sulphur chloride-treated linseed oil, on the other hand, did not show increased alkali resistance.

<sup>97</sup> O. Naumann (German P. 597,209, 1934; *Chem. Abs.*, 1934, 28, 5261) suggests the addition of magnesium oleate to factice oil which is intended as a paint vehicle.

<sup>98</sup> W. T. Branscombe and R. C. L. Everleigh, Canadian P. 281,837, 1928, to Pincin Johnson & Co., Ltd.; *Chem. Abs.*, 1928, 22, 4261. British P. 283,998, 1926; *Brit. Chem. Abs. B*, 1928, 275.

<sup>99</sup> A. Hollander, *Farben-Ztg.*, 1930, 35, 998; *Brit. Chem. Abs. B*, 1930, 382.

<sup>100</sup> E. T. Rydberg, German P. 565,983, 1930; *Chem. Abs.*, 1933, 27, 2599.

<sup>101</sup> D. C. Atkins, U. S. P. 1,575,521, March 2, 1926; *Chem. Abs.*, 1926, 20, 1508. See also J. W.

Phillips, U. S. P. 1,395,242, Oct. 25, 1921; *J.S.C.I.*, 1921, 40, 897A.

<sup>102</sup> German P. 321,264, 1918, to Ballonhüllen-G.m.b.H.; *Chem. Abs.*, 1921, 15, 1083.

<sup>103</sup> O. Brandenberger and A. Riedemann, German P. 596,400, 1934; *Chem. Abs.*, 1934, 28, 4613.

<sup>104</sup> H. Brendel, *Farben-Ztg.*, 1925, 30, 2734; *Chem. Abs.*, 1925, 19, 3603.

<sup>105</sup> J. Osnos and J. Golovistikov, *Moskovo-Zhivovoe Delo*, 1932, 23, 54, 60; *Chem. Abs.*, 1932, 26,

6161. See also S. Vedenkin, *Malyarnoe Delo*, 1931, 3, 26; *Chem. Abs.*, 1932, 26, 5219.

<sup>106</sup> R. Heublyum, *Farben-Chem.*, 1933, 4, 211; *Chem. Abs.*, 1933, 27, 4112.

<sup>107</sup> *Circ., Amer. Paint, Varnish Mfrs.' Assoc.*, 1933, 445, 425; *Chem. Abs.*, 1934, 28, 346. See also G. Fearnley, A. W. Guthrie and J. R. Macauley, *Am. Paint J.*, 1932, 16 (53A), 12, 23, 26; *Chem. Abs.*, 1933, 27, 432.



Besides being used in the preparation of resistant coatings, sulphurized oils are also said to permit of more rapid application of successive coats.<sup>108</sup> The products from the reaction of sulphur chloride on drying oils set throughout the mass and do not depend on the diffusion of oxygen from the surface. Several layers can be applied in quick succession, i.e., three coats in the course of one day or less. The addition of sulphur to drying oils has also been reported to decrease the destruction of their films by atmospheric oxidation.<sup>109</sup> Related to this is the process of Beringer and Zimmer<sup>110</sup> who prevent the congealing of tung oil during heat treatment by the addition of 0.6-1.2 per cent of sulphur or selenium. Even though only a small amount of sulphur is used, heating at 250-300°C. produces a light yellow, nondrying, viscous liquid.

Perry<sup>111</sup> found that films made from sulphur chloride-treated fish oils were unsatisfactory. The unsaturated hydrocarbon squalene,  $C_{30}H_{50}$ , which is one of the constituents of shark-liver oil has also been shown to be not suited for use in paints and, in any event, vulcanization does not improve it.<sup>112</sup> Synthetic drying oils have been prepared by dehydrating crude tall oil<sup>113</sup> with calcined calcium sulphate followed by treating with 5-10 per cent of sulphur monochloride<sup>114</sup> and by esterifying sorbitol with oleic acid.<sup>115</sup> In the latter instance, polymerization of the oil can be effected by heating with sulphur.

Various uses of vulcanized drying oils other than for the preparation of paints and varnishes for the protection of wood, plaster and metal have also been proposed. Thus, Nanfeldt<sup>116</sup> impregnated a brake lining containing asbestos with a sulphur-treated linseed oil. Rubber footwear covered with a soft, tacky, vulcanized varnish have been given a hard finish by treatment with a sulphur halide, sulphuryl chloride or thionyl chloride.<sup>117</sup> Fritz<sup>118</sup> prepared a coating composition for the manufacture of oilcloth by dissolving 4-8 parts of sulphur monochloride in 15 parts of benzine, adding slowly 100 parts of bodied linseed oil followed immediately by 20-30 parts of stand oil. The product was used in linseed- or tung-oil solution.

As early as 1864, Parkes<sup>119</sup> reported that castor oil treated with 2-10 per cent of sulphur chloride could be used as a plasticizer for nitrocellulose. Crane<sup>120</sup> heated cottonseed, olive and castor oils with sulphur (0.11-0.20 of the weight of the oil) at 210°C. The syrupy product was employed in nitrocellulose lacquers. The following formula was stated to give good results as a coating for fabrics and leather:

Butyl acetate . . . . .	7 gallons
Petroleum naphtha . . . . .	3 gallons
Pyroxylin . . . . .	15 pounds
Vulcanized oil . . . . .	30-40 pounds
Pigment . . . . .	1-2 pounds

<sup>108</sup> British P. 288,624, 1927, to Firma Hermann Frenkel; *Chem. Abs.*, 1929, 23, 721. German P. 504,868, 1930; *Chem. Zentr.*, 1930, 2, 2065. Cf. German P. 581,229, 1933, to A.-G. Johannes Jeserich; *Chem. Abs.*, 1933, 27, 5207.

<sup>109</sup> H. A. Gardner and G. G. Sward, *Circ., Am. Paint, Varnish Mfrs.' Assoc.*, 1932, 410, 129; *Brit. Chem. Abs. B*, 1933, 77. See also H. A. Gardner, G. G. Sward and S. A. Levy, *ibid.*, 1931, 388, 218, *Chem. Abs.*, 1931, 25, 4418.

<sup>110</sup> E. Beringer and W. Zimmer, U. S. P. 1,103,473, July 14, 1914, to Reichhold, Flügger & Boecking; *Chem. Abs.*, 1914, 8, 3127.

<sup>111</sup> E. Perry, *Paint, Varnish Prod. Mgr.*, 1933, 9 (10), 26; *Chem. Abs.*, 1933, 27, 5557.

<sup>112</sup> P. Slansky, *Fettechem. Umschau*, 1933, 40, 77; *Chem. Abs.*, 1933, 27, 3091.

<sup>113</sup> See Chapter 36.

<sup>114</sup> B. Föhre, German P. 576,262, 1933; *Chem. Abs.*, 1933, 27, 3835.

<sup>115</sup> British P. 350,992, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1931, 819.

<sup>116</sup> W. Nanfeldt, U. S. P. 1,959,686, May 22, 1934, to World Bestos Corp.; *Chem. Abs.*, 1934, 28, 4551.

<sup>117</sup> British P. 274,357, 1927, to L. Candee & Co.; *Chem. Abs.*, 1928, 22, 2082.

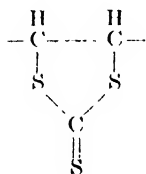
<sup>118</sup> F. Fritz, *Paint, Varnish Prod. Mgr.*, 1934, 10 (4), 28; *Brit. Chem. Abs. B*, 1934, 463.

<sup>119</sup> A. Parkes, British P. 2675, 1864. Castor oil vulcanized by heating at 200-300°C. with 0.1 per cent of selenium has been suggested for the same purpose. W. M. Stanley, U. S. P. 1,955,348, April 17, 1934, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 3921.

<sup>120</sup> F. Crane, British P. 3345, 1891; *J.S.C.I.*, 1892, 11, 446.

The addition of ammonia to nitrocellulose lacquers lowers the viscosity but yields a brittle film. According to Morozov,<sup>121</sup> this brittleness can be partially eliminated if vulcanized oils are used (in admixture with low viscosity nitrocellulose).

Auer and his co-workers<sup>122</sup> have employed sulphurized resins, oils and naphthenic acids in aqueous emulsion as varnishes and impregnating agents. A similar product has been obtained by emulsifying linseed oil and heating at 160-170°C. with colloidal sulphur.<sup>123</sup> The addition of tannic acid to the oil before or after vulcanizing is said to make the sulphurized body more easily emulsified.<sup>124</sup> Guerrey<sup>125</sup> treated a solution of a salt of an unsaturated fatty acid with a solution of sulphur in carbon disulphide and obtained substances which he assumed to have the typical atomic grouping



Aqueous solutions of these products possessed the property of dissolving animal and vegetable fats, oils, waxes and aromatic hydrocarbons. They were used in degumming silk and for leather dressings.

Not only sulphur and sulphur chloride, but also sulphur dioxide, has been employed in the preparation of varnishes and lacquers from drying oils.<sup>126</sup> For example, oxidized drying oils such as linoxyn or oxidized tung oil are treated with sulphur dioxide, or salts derived from it. The products are soluble in water but may be rendered insoluble by heating.

#### FACTICE

One of the principal uses to which vulcanized oils have been put is the preparation of rubber substitutes. Those made from sulphur monochloride are white to yellow in color and are, therefore, called "white factice." They are formed by mixing the two components in the cold. As reaction is rather violent and the mass tends to heat up spontaneously, it is usually carried out with limited quantities of material lest charring take place. At the end of the reaction the hot mass is poured out on a smooth plate from which it can be easily peeled when cold.<sup>127</sup> Since both sulphur and chlorine are found in the product, Henriques<sup>128</sup> presumed that the white factices were addition products of the oils and sulphur chloride. Considerably larger proportions of sulphur chloride are used in making factice

<sup>121</sup> I. R. Morozov, *Zhur. Priklad. Khimn.*, 1931, 4, 117; *Chem. Abs.*, 1931, 25, 5779.

<sup>122</sup> L. Auer and P. Stamberger, *British P.* 321,693, 1928; *Chem. Abs.*, 1930, 24, 2904. Austrian P. 20,047, 1930; *Chem. Zentr.*, 1930, 2, 3350. French P. 686,321, 1929; *Chem. Abs.*, 1931, 25, 618. British P. 321,694; *Chem. Abs.*, 1930, 24, 2904. Austrian P. 20,048, 1930, *Chem. Zentr.*, 1930, 2, 3350. L. Auer and N. Strachovsky, *British P.* 321,699, 1928, *Chem. Abs.*, 1930, 24, 2904. French P. 686,316, 1929, *Chem. Abs.*, 1931, 25, 618. See also P. Stamberger, *British P.* 361,025, 1930; *Chem. Abs.*, 1933, 27, 1120. Hungarian P. 105,074, 1933; *Chem. Abs.*, 1933, 27, 4100.

<sup>123</sup> W. J. S. Naunton, *British P.* 313,252, 1928, to Imp. Chem. Ind., Ltd.; *Brit. Chem. Abs. B.*, 1929, 650.

<sup>124</sup> H. M. Bunbury and R. B. F. F. Clarke, *British P.* 343,533, 1929, to Imp. Chem. Ind., Ltd.; *Brit. Chem. Abs. B.*, 1931, 501.

<sup>125</sup> C. Guerrey, *French P.* 563,214, 1922; *Brit. Chem. Abs. B.*, 1926, 141.

<sup>126</sup> French P. 738,075, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 1773. The products of this reaction can be used also in making inoleum.

<sup>127</sup> T. Seeligmann, G. L. Torrilhon and H. Falconnet, "Indiarubber and Gutta Percha," trans. by J. S. McIntosh; Scott, Greenwood and Son, London, 1910, 261.

<sup>128</sup> R. Henriques, *Chem.-Ztg.*, 1893, 17, 634; *J.S.C.I.*, 1894, 13, 47. The proportions of sulphur and chlorine are not identical with those in sulphur chloride since some hydrogen chloride is lost in the reaction. See E. A. Harvey and H. A. Schuette, *Trans. Wisconsin Acad. Sci.*, 1931, 26, 225, 231, 233; *Chem. Abs.*, 1931, 25, 4726.

than are employed in the case of vulcanized varnishes. Thus, Henriques states that the following amounts of sulphur monochloride give satisfactory results with 100 parts of each of the oils listed:

TABLE 64a.—*Proportions of Sulphur Chloride used with Various Oils.*

Oils 100 Parts	Sulphur Chloride Parts Used
Linseed . . . . .	30
Poppyseed . . . . .	35
Colza <sup>120</sup> . . . . .	25
Cottonseed . . . . .	45
Olive . . . . .	25
Castor . . . . .	20

He points out that there is no relationship between the drying power of the oil and the amount of halide required. Similar observations have been made by Harvey and Schuette.<sup>120</sup> These investigators attempted to develop a method of evaluating oils by treatment with sulphur chloride but found that both the viscosity of the final product and the heat of the reaction were unrelated to the drying power.

The action of sulphur on fatty oils is much slower than that of its chloride. The mixture must be heated before combination takes place. The use of sulphur therefore avoids the accidents which sometimes take place due to the violent action of chloride. The products are dark brown to black in color and are used like the white factices as rubber substitutes and as ingredients in rubber compositions.<sup>121</sup> The preparation of a brown substitute from maize (corn) oil takes place in the following manner:<sup>122</sup> Maize oil (5 parts) is heated to 243°C. and held there for 30 minutes with constant stirring. Melted sulphur (2 parts) is then poured in and when the mass is thoroughly mixed it is run out into a cooling box where it may be stirred.

Knight and Stamberger<sup>123</sup> have studied the interaction of sulphur and triolein. They believed that the course of the reaction was very similar to that observed by Whitby and Chataway<sup>124</sup> in the case of linseed oil. The first product was the result of the simple addition of sulphur and was soluble in acetone. Then the sulphurized molecules condensed with more sulphur to produce an insoluble elastic body. The sulphurized oleic acids formed on hydrolysis were not elastic.

As indicated above, one of the uses to which such products have been applied is the compounding of rubber.<sup>125</sup> Dittmar<sup>126</sup> added soya-bean oil to rubber solutions which were to be vulcanized with sulphur monochloride. The sulphur halide reacted with the oil to form a factice *in situ*. The elongation and suppleness of the vulcanizate was increased. There was, however, a tendency to age poorly and compositions containing more than 20 per cent of oil became worthless in a few

<sup>120</sup> R. Girard and J. Legoute (French P. 700,867, 1929; *Chem. Abs.*, 1931, 25, 3876) used lead tetroxide as a catalyst in the preparation of rubber substitutes from colza oil and sulphur chlorides.

<sup>120</sup> E. A. Harvey and H. A. Schuette, *Ind. Eng. Chem. Anal. Ed.*, 1930, 2, 42; *Ind. Eng. Chem.*, 1931, 23, 675. *Trans. Wisconsin Acad. Sci.*, 1931, 26, 225, 231, 233; *Chem. Abs.*, 1931, 25, 4726.

<sup>121</sup> R. Henriques (*loc. cit.*) bases his analysis of rubber compositions for white and brown factice on the fact that the latter contains sulphur but no chlorine. For the analysis and examination of factice see Grandel and Co., *Kautschuk* 1931, 7, 48; *Chem. Abs.*, 1931, 25, 4441.

<sup>122</sup> T. Seeligmann, G. L. Torrilhon and H. Falconnet, *loc. cit.* See also J. Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," Macmillan and Co., Ltd., London, 1915, III, 190.

<sup>123</sup> B. C. J. G. Knight and P. Stamberger, *J.C.S.*, 1928, 2791. See also P. Stamberger, *Rec. trav. chim.*, 1927, 46, 837; 1928, 47, 973; *Brit. Chem. Abs. B*, 1928, 23; 1929, 26.

<sup>124</sup> G. S. Whitby and H. D. Chataway, *J.S.C.I.*, 1926, 45, 115T.

<sup>125</sup> See W. Alexander (*Kautschuk*, 1924, 10, 18; *Chem. Abs.*, 1924, 28, 4628) for a review of the preparation and use in rubber of white and brown factices.

<sup>126</sup> R. Dittmar, *Gummi-Ztg.*, 1926, 41, 535; *Chem. Abs.*, 1927, 21, 671. H. A. Gardner (U. S. P. 1,446,039, Feb. 20, 1923; *Chem. Abs.*, 1923, 17, 1560) vulcanized a mixture of rubber, benzene and dechlorinated oil with sulphur. (See Chapter 56.)

months. Another way of incorporating the factice is to add it in the form of an emulsion to an aqueous dispersion of rubber.<sup>137</sup>

Some other uses for factice have been suggested. One of these is the preparation of linoleum. A mixture of factice, quartz and the product of sulphur dichloride on linseed oil was recommended for this purpose.<sup>138</sup> Kaufmann<sup>139</sup> replaced the linoxyn ordinarily employed in the manufacture of linoleum with factice, and the customary resin with a synthetic one resulting from the action of sulphur monochloride on naphthalene. It has even been suggested that factice can be used as the intermediate layer in safety glass.<sup>140</sup> Snelling<sup>141</sup> mixed cottonseed oil, carbon disulphide and sulphur chloride and poured the solution on a metallic surface where it was left until hard. The mass was then ground and sulphur chloride mixed with a small quantity of methyl alcohol was added. Liquefaction occurred and the liquid was stirred into an excess of water. A solid separated and this was milled with an equal weight of rosin and the mixture boiled 3 hours in water. The product was used as a gutta-percha substitute. An insecticide has been prepared by heating dichlorobenzene with a vulcanizable oil and sulphur chloride until the mixture sets to a hard mass which is powdered.<sup>142</sup> McCoy<sup>143</sup> considered that factice was a desirable addition to phenol-formaldehyde condensation products. The resulting resins were mixed with plasticizers and fillers and then molded.

A large number of the fatty oils can be used in the preparation of these rubber-like products. Several such substances have already been named. To this list should be added sandal-seed oil<sup>144</sup> and various modified oils. De Waele<sup>145</sup> produced elastic masses by vulcanizing acetylated castor oil or acetylated blown oil with sulphur chloride, sulphur thiocyanate or dithiocyanogen. Hagedorn<sup>146</sup> reports that the moldable material formed by heating the mixed ester of cellulose and phenylacetic, oleic and lauric acids with sulphur at 140°C. is resistant to acids, alkalis and atmospheric oxygen.

Mineral oils are not usually considered vulcanizable. However, Snelling<sup>147</sup> found that rubber-like bodies could be produced from them. He added 20 cc. of methyl alcohol and 50 cc. of carbon disulphide to 100 g. of lubricating oil. One hundred cc. of sulphur chloride were added and the mixture allowed to stand 5 days in a sealed container. The methyl alcohol accelerated the reaction so that at the end of this time a considerable change had taken place in the oil. The liquid was then thoroughly mixed with 500 cc. of water and left in contact with it for 6 days. The excess water and oil were removed by running the resulting mass through rolls. A solid product resulted which was tough and elastic. Oleic acid when treated similarly produced a substitute for lanolin.

<sup>137</sup> German P. 563,164, 1931, to Soc. italiana Pirelli; *Chem. Abs.*, 1933, 27, 1236.

<sup>138</sup> German P. 549,324, 1930, addn. to 484,983, to Deutsche Oelfabrik Grandel & Co.; *Chem. Abs.*, 1932, 26, 4932.

<sup>139</sup> V. Kaufmann, British P. 393,141, 1933; *Chem. Abs.*, 1933, 27, 5995. German P. 591,158, 1934, to Dubois u. Kaufmann G.m.b.H.; *Chem. Abs.*, 1934, 28, 2555.

<sup>140</sup> German P. 563,046, 1931, to Deutsche Oelfabrik Grandel & Co.; *Chem. Abs.*, 1933, 27, 1128. Nonshatterable glass requires a very tough intermediate film such as celluloid to provide satisfactory shock resistance.

<sup>141</sup> W. O. Snelling, U. S. P. 1,479,330, Jan. 1, 1924; *Chem. Abs.*, 1924, 18, 768. See also U. S. P. 1,376,172, April 26, 1921; *Chem. Abs.*, 1921, 15, 2749.

<sup>142</sup> J. Savage, F. Holt and R. Thomas, British P. 361,421, 1930, to Imperial Chem. Ind., Ltd; *Brit. Chem. Abs. B*, 1932, 125.

<sup>143</sup> J. P. A. McCoy, U. S. P. 1,194,201, Aug. 8, 1916; *Chem. Abs.*, 1916, 10, 2594.

<sup>144</sup> M. Sreenivasaya and N. Narayana, *Proc. 15th Indian Sci. Congr.*, 1928, 160; *Chem. Abs.*, 1931, 25, 2868.

<sup>145</sup> A. de Waele, U. S. P. 1,910,005, May 23, 1933, to D. Gestetner; *Chem. Abs.*, 1933, 27, 4113. A. de Waele, British P. 284,415, 1926; *Chem. Abs.*, 1928, 22, 4878.

<sup>146</sup> M. Hagedorn, U. S. P. 1,877,854, Sept. 20, 1932, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 449.

<sup>147</sup> W. O. Snelling, U. S. P. 1,535,740, April 28, 1925; *Chem. Abs.*, 1925, 19, 1968.

Nüth<sup>148</sup> prepared factice by the action of sulphur dichloride<sup>149</sup> on solutions of various oils in benzene and toluene. When heated with an amine, the factice slowly mixes, with the evolution of hydrogen chloride. Thus, samples of factice were prepared using the proportions shown in Table 65.

TABLE 65.—*Factice Preparations.*

Series	Oil		Sulphur Dichloride
A	Linseed	10 parts	3
B	China wood	10	3
C	Poppyseed	10	4
D	Castor	75	6
E	Cod liver	4	1

The resulting bodies were heated at 125-140°C. with the proportions of amines given in Table 66.

TABLE 66.—*Amine-Factice Compositions.*

Factice		Amine	
Linseed	A 1 part	Aniline	3 parts
Linseed	A 1	p-Chloraniline	1
Linseed	A 10	m-Nitraniline	7
China wood	B 1	p-Toluidine	1
China wood	B 1	Monoethyl p-toluidine	4
China wood	B 1	Dimethyl aniline	2
Castor	D 1	Aniline	5
Cod liver	E 1	Aniline	4

When the factice was in solution, a quantity of toluene was added and the amine-hydrochloride precipitate was filtered off. The toluene solution could be used directly as a varnish, or the reaction product could be separated and purified by precipitation and washing with alcohol. If harder materials were desired than those prepared as just described, the latter could be vulcanized by heating with sulphur.

Linseed, cottonseed, castor and other oils react with zinc oxide or hydrated lime when heated to 200°C. to form a product which is hard, but porous and disintegrated by water. Barringer<sup>150</sup> found that the addition of sulphur yields an impervious mass which is not attacked by water. One composition which he used consisted of 20 parts of zinc oxide, 8 parts of sulphur, 40 parts of ground flint, 12 parts of powdered talc, 20 parts of asbestos and 15-20 parts of linseed oil. After thorough mixing, the composition was fashioned into the desired shapes and baked for 4-8 hours at a temperature ranging from 150 to 220°C. Saponification and vulcanization were best carried out at 200-220°C. Although articles made by Barringer's process had a slightly grayish tone instead of the bluish black preferred by molders, they were resistant to water and could be soaked in the latter for weeks with no apparent deterioration.

An earlier composition which consisted of lime, boiled linseed oil, resin and sulphur has previously been mentioned.<sup>151</sup> Ievlev<sup>152</sup> also described the production of plastic bodies. Wood pulp was ground with a drying oil and powdered chalk. Separately, a lime-sulphur was prepared by adding sulphur to lime during the

<sup>148</sup> G. Nüth, U. S. P. 1,159,257 and 1,159,258, Nov. 2, 1915; *Chem. Abs.*, 1916, 10, 296

<sup>149</sup> H. Plauson and J. A. Vielle (British P. 156,143 and 156,144, 1920, *Chem. Abs.*, 1921, 15, 1831, 1832) have vulcanized a factice prepared using sulphur dichloride and obtained an artificial ebonite. The same type of factice was combined by N. Braibant (British P. 374,656, 1922; *Chem. Abs.*, 1923, 27, 3795) with rubber and an abrasive to form a honing composition.

<sup>150</sup> L. E. Barringer, U. S. P. 1,085,102, Jan. 27, 1914, and 1,111,430, Sept. 22, 1914, to General Electric Co.; *Chem. Abs.*, 1914, 8, 1063, 3536.

<sup>151</sup> C. A. Faure, U. S. P. 866,717, July 19, 1887, to Electrical Accumulator Co.

<sup>152</sup> A. I. Ievlev, Russian P. 3429, 1927; *Chem. Abs.*, 1928, 22, 4740.

course of hydration. The two intermediate compositions were mixed and treated with a solution of sodium silicate.

Auer's preparation of varnishes from the action of sulphur and sulphur halides on oils and resins has been mentioned previously. He has also made plastic bodies<sup>108</sup> by similar methods. For example, castor oil was boiled under reduced pressure with metallic calcium until the latter was dissolved and the evolution of hydrogen had ceased. After cooling, the reaction mass was heated to 140°C., mixed with iron oxide, aniline and sulphur, and further heated to 160°C. This product could be molded under pressure.

<sup>108</sup> L. Auer, U. S. P. 1,957,437, May 8, 1934, 1,995,230 and 1,985,231, Dec. 25, 1934, to J. R. Newman; *Chem. Abs.*, 1934, 28, 4272. British P. 239,414 and 289,415, 1927; *Chem. Abs.*, 1929, 23, 727, 722

## Chapter 61

# Resin-Like Materials from Fatty Oils and Miscellaneous Vegetable Oils

Although the polymerization products of the fatty oils are not resins and do not compare in importance with many of the types of resinous products which have been discussed in previous chapters, nevertheless they do comprise a group containing a very wide variety of materials with a correspondingly broad field of applications. No consideration will be afforded here to the numerous compositions which contain heat-treated oils in mere admixture, for the discussion will be confined to those products which fall somewhat vaguely within the category of synthetic resins. The drying and semi-drying oils<sup>1</sup> are notably polymerizable, especially under the influence of catalysts. Chlorination of various fats and oils yields rubber-like polymers, and insulating compositions result from the polymerization of castor oil. A novel and very interesting development has been the introduction of the use of cashew-shell oil for the preparation of resinous materials.

### TUNG OR CHINA WOOD OIL

Reference<sup>2</sup> has already been made to the employment of tung oil (China wood oil) with rosin, ester gums and other like materials. Substances resulting from the utilization of tung oil itself are now to be discussed.

The gelatinization of tung oil on strong heating is a familiar change, the chemistry of which has been investigated to some extent. Marcusson<sup>3</sup> studied the nature of the coagulation phenomenon, and, from solubility tests of heated tung oil, concluded that gelatinized oil contains 3 constituents besides oxidation products and anhydrides: (1) unchanged oil, (2) an oily polymerization product and (3) a solid polymerization product, the amounts of each varying according to the conditions of heating.<sup>4</sup>

Tung oil contains chiefly the glyceride of eleostearic acid with a small proportion of oleic and stearic glycerides.<sup>5</sup> The first of these acids is triply unsaturated, and is responsible for the characteristic properties of the oil. The polymerization of tung oil is assumed<sup>6</sup> to involve the eleostearic radical. The more highly polymerized molecules are less soluble in acetone, and consequently the matter insoluble in acetone increases rapidly with the temperature of heating. Accordingly, tung oil treated at relatively low temperature has greater ease of flow, can be thinned out to a larger extent, and produces a more elastic film. In contrast with

<sup>1</sup> For further information regarding the chemistry of film formation of drying and semi-drying oils, particularly linseed oil, see J. S. Long, A. E. Rheineck and G. L. Ball, *Ind. Eng. Chem.*, 1933, 25, 1086. G. W. Ellis, *J.S.C.I.*, 1925, 44, 401T. F. Ohi, *Farbe u. Lack*, 1934, 554; *Chem. Abs.*, 1935, 29, 945.

<sup>2</sup> See Chapters 19, 27, 39 and 44.

<sup>3</sup> J. Marcusson, *Z. deut. Oel.-Fett-Ind.*, 1923, 43, 162; *Chem. Abs.*, 1923, 17, 2198.

<sup>4</sup> The difference in refractive indices of tung oil and its unpolymerisable fraction, being a constant, is the basis of a test for adulterants (vegetable tallow, rape or poppy-seed oil and rosin). F. Cheng, *Trans. Sci. Soc. China*, 1934, 8, 97; *Science (China)*, 1934, 18, 758; *Chem. Abs.*, 1935, 29, 362.

<sup>5</sup> For a discussion of the characteristic acids of drying oils see J. Bössekens, *Chem. Weekblad*, 1934, 31, 418; *Chem. Abs.*, 1935, 29, 2002.

<sup>6</sup> L. A. Jordan, *J.S.C.I.*, 1934, 53, 1T.

this, oil treated at a higher temperature does not have such good brushing qualities, but the film, when prepared, is more durable.

Tung oil contains 80-85 per cent of  $\alpha$ -eleostearic glyceride, and this is completely converted into the  $\beta$ -isomer in the presence of catalysts. Each form can be readily isolated.<sup>7</sup> It has been stated that stand oils made from  $\alpha$ -tung oil do not differ perceptibly from those from the  $\beta$ -oil.<sup>8</sup> Maleic anhydride adds to the conjugated unsaturation of each isomer but, according to Morrell, Marks and Samuels,<sup>9</sup> only the addition product with  $\beta$ -eleostearin produces films which can be hardened by heat. Thus, in this instance, the thermal-hardening property is taken to be related to the stereo-isomeric structure. Rossmann<sup>10</sup> believed that a cyclization phenomenon accompanies tung oil polymerization, and the product is a mixture of monomeric and dimeric 5-butyl-1,3-cyclohexadien-6-caprylic acid.

Köhler<sup>11</sup> has studied the cooking of tung oil at 280° and 320°C. The product obtained at 280°C. was the more satisfactory for use with resins in lacquers. The less viscous oils, prepared at lower temperatures, are best used, according to Köhler, with linseed stand oil. Friction blocks may be made by saturating asbestos pulp or woven fabric with an oil binder such as tung oil and subjecting the product to heat and pressure.<sup>12</sup>

Condensation products are formed when tung oil is treated with phenols in the presence of sulphuric acid.<sup>13</sup> Baekeland<sup>14</sup> devised a process whereby tung oil is heated at 205-210°C., without solidification, mixed with a filler (wood flour, asbestos or silic), and the mixture molded and baked. The molded articles are given a coat of asphalt or phenolic condensation products. Electrical insulators may be made in this manner. Tung oil can also be polymerized in the presence of hydrocarbon oils.<sup>15</sup>

For the production of satisfactory varnishes it is often desirable that the gelatinization be retarded, and this is accomplished by the addition of various substances. Rhodes and Potts<sup>16</sup> found the following order of efficacy in this respect: glycerol, oleic acid, rosin, ester gum, cumarone resin and linseed oil. The presence of only 6 per cent of glycerol prevented gelatinization of the oil. This mixture with the addition of lead linoleate, heated to 280°C. until sufficiently bodied and then thinned with turpentine gave rapid drying, smooth, tough, transparent films. The addition of rosin, naphthenic acids or linseed oil to tung oil to avoid its coagulation during heating does not, according to Marcussen,<sup>17</sup> stop polymerization, but merely hinders gel formation. The gelatinization of tung oil may be delayed by heating it with glycerol to a point short of gelatinization and cooling by adding cold rosin oil. The composition is made quick-baking by the addition of a metal soap, such as manganese linoleate, or of a polymerized but ungelatinized resin glyceride, which may be produced by heating a mixture of glycerol and a resin (Congo copal) with rosin oil. The composition after application to a metallic article is hardened by the action of heat, which

<sup>7</sup> A. W. Thomas and J. C. Thomson, *J.A.C.S.*, 1934, 56, 898. A. Dingwall and J. C. Thomson, *ibid.*, 899.

<sup>8</sup> H. Ulrich, *Farben-Ztg.*, 1934, 39, 704; *Brit. Chem. Abs.* B, 1934, 769.

<sup>9</sup> R. S. Morrell, S. Marks and H. Samuels, *J.S.C.I.*, 1933, 52, 130T.

<sup>10</sup> E. Rossmann, *Fettchem. Umschau*, 1933, 40, 96. See also R. L. Houck, *Paint, Oil, Chem. Rev.*, 1928, 86 (21), 10; *Chem. Abs.*, 1929, 23, 5336. J. van Loon, *Chem. Weekblad*, 1934, 31, 419; *Chem. Abs.*, 1935, 29, 2002.

<sup>11</sup> F. Köhler, *Farbe u. Lack*, 1933, 67. *Brit. Chem. Abs.* B, 1933, 275.

<sup>12</sup> I. J. Novak, *British P.* 354,889, 1930; *Chem. Abs.*, 1932, 26, 4144.

<sup>13</sup> *British P.* 310,562, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1929, 636. See Chapter 19.

<sup>14</sup> L. H. Baekeland, *U. S. P.* 1,312,093, Aug. 5, 1919, and 1,372,114, March 22, 1921; *Chem. Abs.*, 1919, 13, 2579; 1921, 15, 1975.

<sup>15</sup> P. A. McCoy, *U. S. P.* 1,894,626, Jan. 17, 1933; *Chem. Abs.*, 1933, 27, 2591.

<sup>16</sup> F. H. Rhodes and T. J. Potts, *Chem. Met. Eng.*, 1923, 29, 533; *Chem. Abs.*, 1923, 17, 3796.

<sup>17</sup> J. Marcussen, *loc. cit.*



drives off the rosin oil from the polymerized material.<sup>18</sup> The addition of thymol and  $\beta$ -naphthol to tung and linseed oil was found by Hilpert and Niehaus<sup>19</sup> to retard polymerization.

When exposed to ultraviolet light or treated with small quantities of iodine, sulphur chloride, sulphur or ozone, tung oil changes to a solid, the  $\beta$ -form. The latter can be heated at 260°C. to secure a gasoline- or naphtha-soluble resin adaptable for varnishes.<sup>20</sup>

Bürstenbinder<sup>21</sup> considered that the action of the majority of the retarding substances is purely mechanical. The effect of sulphur on the heated oil is, however, an exception. Even as little as 0.01 per cent of sulphur has a decided retarding action on the drying of the oil.

Gardner<sup>22</sup> reduced the iodine number of tung oil, and hence its tendency to dry rapidly with the formation of brittle, "frosted" films, by heating to 290°C. with a small amount of sulphur (0.05 per cent) or an organic sulphur compound. Addition of a heavy metal or metal oxide (lead, copper or zinc) effects desulphurization of the oil when hot, leaving a product of less unsaturation than the original substance but with improved coating properties. Selenium is reported to be related to sulphur in its action.

When tung oil is heated very rapidly, as can be accomplished by passing it through a heated coil, it may be brought to a temperature exceeding 300°C. without gelatinization taking place, and such "thermolyzed" oil is used commercially as a constituent of varnishes and nitrocellulose lacquers.<sup>23</sup>

Thauss and Mauthe<sup>24</sup> found that tung oil and phenol react in the presence of dilute sulphuric acid, and that on treating the product with concentrated sulphuric acid (which acted as a sulphonating agent), a resinous substance was formed soluble in alkalis and suitable for treating textile materials. The oil may also be heated with 2-naphthol-6-sulphonic acid and dilute sulphuric, to yield a thick condensation product.<sup>25</sup> Marcusson found that treatment of tung oil with nitric or sulphuric acid causes polymerization to a solid substance. Linseed and other fatty oils give no separation of solid with nitric acid, and the reaction is therefore adapted for distinguishing tung from other oils.<sup>26</sup> A similar test with a drop of sulphuric acid (concentrated) serves to detect 10 per cent or more of tung oil in raw, boiled or blown linseed oil.<sup>27</sup> A thickening oil for lacquers is made by heating tung oil to 300°C. with acetic acid and nitrosodiphenylamine in the absence of oxygen.<sup>28</sup> The use of tung oil in aqueous colloidal solution has been suggested.<sup>29</sup>

Hydrogenated tung oil was used by Seigle<sup>30</sup> to impregnate asbestos brake shoes or linings, which were later exposed to a temperature at which polymerization of the oil occurs. Tung oil, hydrogenated until its iodine number has fallen to 120-130, is used with or without the addition of a small percentage of gilsonite

<sup>18</sup> C. D. Hocker, U. S. P. 1,634,359, July 5, 1917; *Chem. Abs.*, 1927, 21, 2993 British P. 238,696, 1924, to Western Electric Co., Ltd.; *J.S.C.I.*, 1925, 44, 890.

<sup>19</sup> R. S. Hilpert and C. Niehaus, *Z. angew. Chem.*, 1934, 47, 86; *Chem. Abs.*, 1934, 28, 2549.

<sup>20</sup> C. G. Gauerke, British P. 312,052, 1928, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1930, 24, 980. See Chapter 44.

<sup>21</sup> R. Bürstenbinder, *Farben-Ztg.*, 1917, 23, 243; *Chem. Abs.*, 1919, 13, 2139.

<sup>22</sup> H. A. Gardner, U. S. P. 1,986,571, Jan. 1, 1935; *Chem. Abs.*, 1935, 29, 1270.

<sup>23</sup> F. M. Reece, U. S. P. 1,903,686 and 1,903,686, Apr. 11, 1933, to O'Brien Varnish Co.; *Chem. Abs.*, 1933, 27, 3350.

<sup>24</sup> A. Thauss and G. Mauthe, U. S. P. 1,779,345, Oct. 21, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 224. German P. 536,550, 1927; *Chem. Abs.*, 1932, 26, 1137.

<sup>25</sup> A. Thauss and H. Keppler, German P. 538,762, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 2200. See also British P. 346,425, 1930; *Brit. Chem. Abs. B*, 1931, 684.

<sup>26</sup> J. Marcusson, *Farben-Ztg.*, 1932, 37, 1354; *Chem. Abs.*, 1932, 26, 4725.

<sup>27</sup> Z. Leppert and Z. Majewski, *Przemysł Chem.*, 1934, 18, 471; *Brit. Chem. Abs. B*, 1935, 159.

<sup>28</sup> F. Pillnay, German P. 560,702, 1929; *Chem. Abs.*, 1933, 27, 1217.

<sup>29</sup> French P. 752,223, 1933, to Elektrochemische Werke München A.-G.; *Chem. Abs.*, 1934, 28, 917.

<sup>30</sup> W. R. Seigle, U. S. P. 1,486,363, Nov. 21, 1922; *Chem. Abs.*, 1923, 17, 618.

for impregnation, the temperature of the impregnated material being raised to 240°C. to effect polymerization.

#### TUNG OIL AND METALLIC CHLORIDES

Scobel<sup>21</sup> made use of the reaction between tung oil and anhydrous chlorides. On grinding anhydrous ferric chloride or its hydrates with the oil, a solid is produced which is non-coherent, yellow in color, and which gradually darkens. When the ferric chloride is ground in an indifferent oil (such as rosin oil or linseed oil) and then quickly mixed with tung oil, a homogeneous mass is formed. If allowed to solidify in molds, these products retain the shape of the container. The solidification is accompanied by a perceptible increase of temperature and volume. The molded articles are very glossy and jet black in appearance. They are opaque except when in thin sections. When first removed from the mold or container, the solid substance is slightly tacky, but soon loses this property on exposure to the atmosphere, or when kept at a temperature of 90-100°C. for a few hours. Prolonged exposure to elevated temperatures has a hardening effect on the mass. The outer portions, which are in contact with the atmosphere, become very much firmer than the interior. With zinc chloride the solid products are brown to deep red and sometimes they are translucent. Aluminum chloride gives a very deep brown to black color.

In the polymerization of tung oil by metallic chlorides, rosin and ester gum or other oil-soluble resins<sup>22</sup> can be employed up to 40 per cent by weight of the tung oil used. When quantities in excess of 40 per cent are employed the product is deficient in resiliency, is quite brittle and softens at somewhat above room temperature.

Tung oil fatty acids can be solidified by active chlorides in anhydrous solvents, but preferably in conjunction with the raw or blown oil itself. Specimens of oil which have been partially polymerized are unsuitable because products solidified from these oils soften and grow sticky at comparatively low temperatures. Tung oil which has been heated above the polymerization point with small amounts of sulphur can be solidified in the usual manner.

One kilogram of tung oil alone requires 25 cc. of a 20 per cent solution of ferric chloride in anhydrous acetone to cause solidification. As much as 150 cc. can be used on that quantity of oil to make a firmer product.<sup>23</sup> Tung oil containing rosin or ester gum requires somewhat larger amounts of ferric chloride in solution. Usually most additions such as rosin, wood flour, cork and other fillers and pigments exercise a retarding influence on solidification, and it is found desirable to use larger amounts of ferric chloride solution or stronger solutions in such compositions.

A formula suggested for making slabs for tile or flooring is: 8 kg. of tung oil and 2 kg. of rosin are dissolved by warming and ground with 1½ kg. each of infusorial earth, wood or cork flour and oxide of iron (red), to which is added 1 kg. of a solution of ferric chloride in acetone (made from equal parts by weight of hydrated ferric chloride and anhydrous acetone). Another formula is: 1 kg. of tung oil containing 40 per cent rosin, 0.5 kg. of tung oil containing 10 per cent ester gum, 50 g. cork meal, 50 g. wood flour, 100 g. Indian red, 200 g. magnesium silicate or other mineral filler and 100 cc. of a solution made from 1 kg. of ferric chloride and 1/3 kg. of anhydrous acetone.

<sup>21</sup> B. Scobel, U. S. P. 1,833,864, July 5, 1921; *Chem. Abs.*, 1921, 15, 3758.

<sup>22</sup> E. Lichtenstern (U. S. P. 1,720,487, July 9, 1929; *Chem. Abs.*, 1929, 23, 4321) found that on heating asphalt (containing not more than 10 per cent of a condensing agent such as ferric chloride, zinc chloride or aluminum chloride) to 270-280°C. and mixing with a quantity of tung oil not exceeding that of the asphalt used, an infusible mass is formed on further heating which may be used on roads, floors or for treating pasteboard.

<sup>23</sup> Twenty cubic centimeters of a saturated solution of ferric chloride in ether when stirred into 1 gallon of raw tung oil will cause it to gel in 30 minutes. *Circ., Am. Paint Varnish Mfrs. Assoc.*, 1929, 342, 66, 66.

Stannic chloride (anhydrous) in cooled anhydrous acetone also produces an active solidifying solution. The pure fuming anhydrous chlorides of tin or antimony cannot be used without such a solvent, for their action on the oil is too energetic, causing clotting or non-uniform solidification.

According to Marcusson,<sup>54</sup> anhydrous stannic chloride is a catalyst for the polymerization of tung, linseed and fish-liver oils. The polymerized fatty acids from tung oil could be separated into (1) solid acids (acid value 186, saponification value 199.5, iodine value 81), yielding sodium salts soluble in water but insoluble in alcohol, and (2) pale, unimolecular, semi-liquid acids soluble in light petroleum ether and forming sodium salts soluble in alcohol. Oleic acid treated with aluminum chloride in the cold is also converted into a solid mass, slightly elastic when broken.<sup>55</sup>

Tung oil, and other unsaturated oils, may be made water-soluble by treating their oxyns with sulphur dioxide and alkali. Such water solutions yield resinous products upon treatment with inorganic chlorides.<sup>56</sup> It has been suggested that inorganic halides catalyze rearrangement of the double bonds in unsaturated glycerides.<sup>57</sup> Polymerization of tung oil occurs in the presence of zinc chloride and acetone peroxide.<sup>58</sup> Adulterants delay the time required for catalytic solidification.<sup>59</sup>

#### TUNG OIL AND AROMATIC AMINES

Lilienfeld<sup>40</sup> has made resinous compositions by heating tung oil with toluidine and a condensing agent. A hardening effect may be obtained by treatment with formaldehyde. A product of a resinous nature is obtained by heating one kg. each of o-toluidine and tung oil with 150-200 g. of zinc chloride in 60-100 g. water. The temperature is maintained between 200° and 300°C. until a satisfactory degree of resinification is reached. When employing formaldehyde the following procedure is recommended: 1 kg. tung oil mixed with 1 or 2 kg. of o-toluidine is heated to 80°C. and 110 g. of zinc chloride dissolved in an equal weight of water added. The temperature is slowly raised while agitating the mixture and the excess of toluidine which distils is collected. The temperature of the heating bath is gradually raised to 260-290°C. and is maintained in this neighborhood until the mass becomes hard and resin-like on cooling. The resinified material is washed by kneading with water and is heated gradually with 20-200 g. of aqueous formaldehyde or an equivalent amount of trioxymethylene. A modification of the process involves adding the formaldehyde with the toluidine.

Auer<sup>41</sup> found that resins were formed when linseed, tung, or castor oils were heated above 200°C. with primary aromatic diamines. These products were suggested for use as varnishes. By the incorporation of an alkali, followed by vulcanization, rubber substitutes are formed. Resins are also prepared by condensing tung oil with polynuclear methylenic compounds of aromatic amines.<sup>42</sup> Solvents and condensing agents could be employed and hardening attained by aldehyde treatment. For example, a thick oil was formed from tung oil, aniline

<sup>54</sup> J. Marcusson, *Chem. Umachau*, 1929, 36, 53; *Brit. Chem. Abs.* B, 1929, 292. See also H. A. Bruson and H. Staudinger, *Ind. Eng. Chem.*, 1926, 18, 381.

<sup>55</sup> N. D. Zelinskii and K. P. Lavrovski, *Ber.*, 1928, 61, 1054; *Chem. Abs.*, 1928, 22, 2920.

<sup>56</sup> British P. 402,759, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3254.

<sup>57</sup> R. Zschunke, *Dis.*, Leipzig, 1931; *Chem. Abs.*, 1934, 28, 1777.

<sup>58</sup> W. B. Stoddard, T. H. Geiger and L. M. Burgess, U. S. P. 1,924,524, Aug. 29, 1933, to Tung Oil Products Co.; *Brit. Chem. Abs.* B, 1934, 545.

<sup>59</sup> M. Th. Francois, *Bull. sci. pharmacol.*, 1934, 41, 269; *Chem. Abs.*, 1934, 28, 4921.

<sup>40</sup> L. Lilienfeld, U. S. P. 1,037,188, Aug. 27, 1912, and 1,090,730, Mar. 17, 1914; *Chem. Abs.*, 1912, 6, 3333; 1914, 8, 1680. British P. 15,657, 1912; *Chem. Abs.*, 1914, 8, 265. French P. 417,392, 1910; *J.S.C.I.*, 1911, 30, 36.

<sup>41</sup> L. Auer, British P. 337,732, 1929; *Brit. Chem. Abs.* B, 1931, 238.

<sup>42</sup> French P. 770,400, 1934, to Soc. pour l'ind. chim. & Bâle; *Chem. Abs.*, 1935, 29, 524. See Chapter 33.

and aniline hydrochloride. This was heated with anhydroformaldehydeaniline for 1-2 hours at 200°C., then treated with formaldehyde.

Tests have been carried out in the author's laboratory on the production of resins from tung oil, and aniline, p-toluidine or xylidene. Thus, 50 parts of oil and 50 parts of aniline were placed in a round bottom flask with 10 parts of zinc chloride dissolved in 5 parts of water. The flask was connected with a condenser and gradually heated. Vigorous frothing occurred between 100° and 120°C. and a small amount of water was distilled out. On further heating to 200°C. the liquid boiled quietly and was of a light yellow color. A slight quantity of oily substance was distilled off during this period. At 210°C., a second frothing took place and the substance began to darken, while water and a small amount of oil distilled. At 280°C., the substance was still liquid and could be easily poured out of the flask. On cooling it gave a reddish-brown resin, but on further heating, the mass solidified inside the flask forming a spongy, sticky, resinous body, less fusible than the resin obtained from the solution heated only to 280°C. The yield of resin amounted to 70 per cent of the total weight of material taken. The product obtained at 280°C. is of good transparency and brittle, but slightly tough, when cold. It does not harden even on heating for several hours. Some of its properties, together with those of similar resins from p-toluidine and xylidene, are shown in Table 67.

TABLE 67.—*Properties of Tung Oil-Amine Resins.*

Properties	Aniline	Resin from Tung Oil and p-Toluidine	Xylidene
Melting point . . . . .	115-120°C.	65-70°C.	41-43°C.
Test on hot plate . . . . .	Gummy	Tarry	Thick liquid
Heating with 20% of paraform	Hardened in 3 minutes	Gummy in 4 hours	No effect
Solubilities			
Alcohol . . . . .	Insoluble	Soluble warm	Soluble
Benzene . . . . .	Insoluble	Slightly soluble warm	Partly soluble
Acetone . . . . .	Slightly soluble warm	Soluble	Soluble
Ether . . . . .	Insoluble	Insoluble	Difficultly soluble
Alcohol-Benzene . . . . .	Partly soluble warm	Soluble warm	Easily soluble
Alcohol-Acetone . . . . .	Partly soluble warm	Soluble warm	Soluble

#### CHLORINATED OILS AND FATS

A general procedure for preparing resin substitutes by exhaustive chlorination of various organic substances, proposed by Boehringer,<sup>44</sup> involves dissolving the substance (an oil, fat, wax or rosin) in carbon tetrachloride and treating the solution with chlorine gas. An increase in temperature accompanies the first stage of chlorination, but later a drop in temperature occurs. Chlorination is continued far beyond this point, exposure to actinic light serving to reduce the time required for the reaction. Chlorinated paraffin and ceresin wax show a notable resistance to the action of strong acids.<sup>44</sup> Colorless oils or sticky, plastic solids, useful as dyeing assistants, are formed in the chlorination or bromination of fatty acids (above C<sub>8</sub>).<sup>45</sup> The free halogen or a mixture of chlorate and hydrochloric acid may be employed. Ricinoleic acid gives products containing 3, 6, 7 or 16 atoms of chlorine; oleic acid takes up 3 or 4; stearic acid, 6; and dihydroxystearic acid, 5 atoms of chlorine. Treatment of these chlorinated derivatives with strong alkalis yields alkali-soluble products, proposed as cleansing and emulsifying agents. On boiling with sodium hydroxide, rubber-like polymers are obtained.<sup>46</sup>

<sup>44</sup> German P. 256,856, 1910 and 258,156, 1911, to C. F. Boehringer & Söhne; *J.S.C.I.*, 1913, 32, 499, 613.

<sup>45</sup> For particulars of the chlorination of waxes and oils see Chapter 56.

<sup>46</sup> British P. 336,623, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1931, 149.

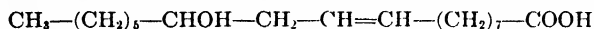
<sup>46</sup> British P. 340,011, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2737. See also British P. 342,761, 1929; *Brit. Chem. Abs.* B, 1931, 450.

When tung oil is treated with chlorine until the reaction has somewhat abated and the temperature begins to fall, a body containing about 28 per cent of chlorine is obtained. This product is a thick, dark liquid and splits off hydrochloric acid continuously on standing at room temperature.<sup>47</sup> Further chlorination in carbon tetrachloride solution yields a solid, transparent substance.<sup>48</sup>

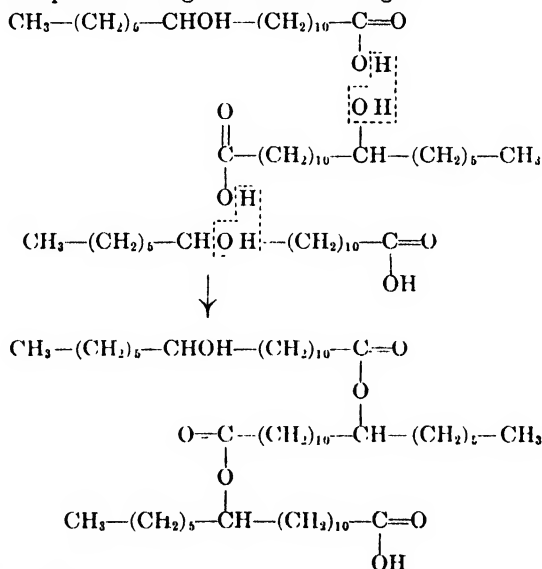
The drying power of tung or soya-bean oil is improved by mixing the oil with about 20 per cent dry calcium hypochlorite and heating at 60-70°C.<sup>49</sup> Another procedure which may be used is to heat the drying oil (tung, etc.) with a chlorine-containing organic compound or with a so-called "dechlorinated mineral oil." Thus, fatty oils were heated with chlorinated fats or with p-toluene sulphonyl chloride and were converted into products of the stand-oil type.<sup>50</sup> Gardner<sup>51</sup> has found that "dechlorinated oils" (mineral oil, chlorinated, and then treated for the elimination of chlorine) facilitate the gelatinization of tung oil. The product is extremely resistant to most chemical reagents.

### CASTOR OIL.—ESTOLIDE FORMATION

Castor oil,<sup>52</sup> as is well known, consists essentially of the glyceryl ester of ricinoleic acid.<sup>53</sup> Hydrolysis of the oil yields ricinoleic acid of the structure



By the hydrogenation of castor oil 12-hydroxystearin is formed. Hydrolytic cleavage of this stearin does not set free the simple 12-hydroxystearic acid but, rather, these molecules re-esterify intermolecularly. The carboxyl group of one molecule condenses with a hydroxyl group of another and the reaction leads to the formation of compounds of higher molecular weight.



<sup>47</sup> C. F. Boehringer & Sohne, *loc. cit.*

<sup>48</sup> Linseed oil behaves in the same manner. Cotton oil is more heavily chlorinated by exposure to light during the process. See also French P. 433,415, 1911, and 459,261, 1912; *J.S.C.I.*, 1912, 31, 290A; 1913, 32, 1120A.

<sup>10</sup>L. D. Taylor, U. S. P. 1,861,514, June 7, 1932, to Mathieson Alkali Works; *Brit. Chem. Abs. B*, 1933, 477.

<sup>50</sup> German P. 585,187, 1933, to Firma L. Blumer; *Chem. Abs.*, 1934, 28, 1562.

<sup>51</sup> H. A. Gardner, U. S. P. 1,463,883 and 1,463,884, Aug. 7, 1933; *Chem. Abs.*, 1923, 17, 3260.

<sup>24</sup> See also Chapter 43.

<sup>55</sup> According to A. Heiduschka and G. Kirsten (*Pharm. Zentralhalle*, 1930, 71, 81; *Chem. Abs.*, 1930, 24, 1933) the other acids are oleic,  $\alpha$ -linoleic, stearic and dihydroxytearic. See also E. Eibner and E. Münzing, *Chem. Umschau*, 1925, 32, 166; *Chem. Abs.*, 1925, 19, 3027.

These long ester chains are termed *estolides* and may in turn be re-esterified with glycerol yielding polyester fatty acid glycerides of very high molecular weight; complexes of 12,000 and over have been prepared. These are viscous at room temperature, salve-like in the cold and liquid at elevated temperatures.<sup>54</sup> They have valuable technical properties as lubricants and as flexibilizing agents in the textile and leather industry.<sup>55</sup> Saturation of the oil, as by hydrogenation, is not essential to the formation of estolides.

Dihydroxystearic acid according to Bauer and Eberle<sup>56</sup> condenses at 200°C. to an estolide which, from its acid number, must represent at least a 5-fold condensate. At 300°C. the estolide breaks down again into dihydroxystearic acid and ketostearic acid; the latter is formed by ketolization of the 10-hydroxyoleic acid (10-hydroxy-9-octadecenoic-1-acid). By the action of zinc chloride on oleic acid in acetic acid solution, iso-oleic (10-octadecenoic acid) and dihydroxystearic acid were obtained. The latter could be distilled in a vacuum but at 200°C. reverted to an estolide.<sup>57</sup>

Estolides derived from saturated hydroxy acids, and their esters with mono- or polyhydric alcohols find application for oiling artificial fibers of cellulose derivatives.<sup>58</sup> By treating cellulose, or cellulose derivatives containing at least one reactive hydroxyl group with the chloride of an estolidic acid, and a fatty acid chloride, there result products resembling cork.<sup>59</sup> Thus, cellulose, lauryl chloride, chlorobenzene, polyricinyl chloride and pyridine are heated at 125-130°C. for 90 minutes. The product can be molded under pressure when hot.

Wittka<sup>60</sup> found that by heating ricinoleic acid to 180°C. in the presence of naphthene-sulphonic acid with addition of castor oil until saturation is reached, a thick viscous oil is obtained which is the glycerol ester of polyricinoleic acid.

Estolide formation probably underlies the production of lubricants by heating castor oil to 200°C., and introducing glycerol under pressure<sup>61</sup> and the preparation of esters of high viscosity from castor oil by the method of Del-Turco.<sup>62</sup> Castor oil is partially hydrolyzed until the acid number is 80-120, and the washed acid heated to 250°C. in vacuum, with or without a catalyst, to effect auto-condensation. Raw castor oil is then added to reduce the acid number below 6, yielding a product soluble in mineral oils.

The mutual solubility of castor oil and gasoline is found to vary considerably with the composition of the latter. Olefinic, aromatic or naphthenic hydrocarbons are miscible in all proportions whereas the solubility of the paraffins is limited.<sup>63</sup> By heating castor oil with higher fatty acids *in vacuo* (to 230°C. with oleic or to 220°C. with stearic), oils are produced which are soluble in petroleum hydrocarbons.<sup>64</sup> Estolides, in conjunction with drying and semi-drying oils, may be used to prepare sizing for textiles.<sup>65</sup> Castor oil may also be heated with hydrocarbon derivatives whose boiling point is near the polymerization temperature so that they distil off during the process.<sup>66</sup>

<sup>54</sup> A. Grün, *Chem. Umschau Fette Oele Wachse, Harze*, 1925, 32, 225; *Chem. Abs.*, 1926, 20, 305. See also Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, 945. Also L. Light, *Paint, Varnish Prod. Mgr.*, 1934, 11 (3), 14, *Chem. Abs.*, 1934, 28, 6578.

<sup>55</sup> Cf. *Chem. Age (London)*, 1928, 18, 262.

<sup>56</sup> K. H. Bauer and A. Eberle, *Z. angew. Chem.*, 1930, 43, 902; *Chem. Abs.*, 1931, 25, 489.

<sup>57</sup> K. H. Bauer and P. Panagoulas, *Chem. Umschau*, 1930, 37, 189; *Brit. Chem. Abs. A*, 1930, 1162.

<sup>58</sup> German P. 525,299, to Aceta G.m.b.H.; *Chem. Abs.*, 1931, 25, 4136.

<sup>59</sup> British P. 300,207, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 3573.

<sup>60</sup> F. Wittka, Swiss P. 151,317, 1930; *Chem. Abs.*, 1932, 26, 4825.

<sup>61</sup> G. Komada, Japanese P. 91,871, to Sakae Katura; *Chem. Abs.*, 1932, 26, 1771.

<sup>62</sup> C. R. Del-Turco, U. S. P. 1,936,831, Nov. 28, 1933, to French Society Legendre Vin & Guetet; *Chem. Abs.*, 1934, 28, 1048. German P. 559,756, 1931; *Chem. Abs.*, 1933, 27, 836. British P. 385,021, 1931; *Chem. Abs.*, 1933, 27, 4484.

<sup>63</sup> G. H. Taber and D. R. Stevens, *Ind. Eng. Chem.*, 1928, 20, 1185.

<sup>64</sup> German P. 452,634, 1925, to Chem. Fabr. Flörsheim H. Noerdlinger; *Chem. Abs.*, 1930, 24, 519.

<sup>65</sup> British P. 871,048, 1961, to Aceta G.m.b.H.; *Brit. Chem. Abs. B*, 1932, 597.

<sup>66</sup> German P. 548,716, 1927, to J. Simon & Dürkheim; *Chem. Abs.*, 1932, 26, 4195.

The polymerization of castor oil in the presence of metallic oxides yields a composition for coating wire which, according to Harris,<sup>67</sup> can be solidified in contact with the wire by heating to about 300°C. for 3 minutes or less. Copper, ferric or aluminum oxide or alkaline earth oxides are heated with castor oil at 240-310°C. until 5-15 per cent of the castor oil has distilled. Metallic resins and fossil resins also may be employed.<sup>68</sup> Boiled castor oil has found use as a protective coating for metals.<sup>69</sup> A composition that remains flexible comprises oxidized and polymerized castor oil, 60, aluminum oxide, 5, mica, 15, and asbestos 15 parts. The temperature should be above 150°C. during the incorporation of aluminum oxide.<sup>70</sup> Castor oil is rendered more viscous, as well as soluble in mineral oils, by heating with tin oxide at 200-250°C. for 8-12 hours.<sup>71</sup>

Substances resembling tung oil are obtained by heating castor oil at 270-280°C. while it is stirred in air, toluene sulphonyl chloride being employed as a catalyst. The products may be used for making lacquer.<sup>72</sup> Also, the oil may be heated at 200-250°C. in the presence of a substance which retards thickening (rosin, synthetic resin, sulphur, etc.) until the acid number reaches 30 or less. The liquid now somewhat resembles tung oil, and is useful in the manufacture of paints.<sup>73</sup> Heated at 200-260°C. with a small amount of phosphoric acid or of an organic phosphate, castor oil becomes soluble in mineral oil, and on prolonged treatment acquires drying properties resembling those of linseed and tung oil. It may be used as a lubricant or in paints.<sup>74</sup>

Castor oil heated at 100°C. for 1 to 3 hours with concentrated selenious acid yields a rubber-like mass which is insoluble in alcohol, ether, benzene and pyridine. This material is saponifiable with alcoholic potash. When treated with alcohol or ether it swells to a jelly which dries to a solid that can be pulverized.<sup>75</sup> Polymerization can also be accomplished by means of nitric acid: if castor oil at 47.5°C. is treated with 1/80 of its weight of concentrated nitric acid, and the temperature is raised to 116°C., solidification occurs.<sup>76</sup> Nitrated castor oil has been used with nitrocellulose under the trade name of "Velvrl." Such mixtures are homogeneous in all proportions and have been used as artificial rubber.<sup>77</sup> Similar products have been proposed as constituents of explosives.<sup>78</sup> A binding material has been prepared by Cadoret<sup>79</sup> from saponified oils by oxidation with nitric acid and subsequent further saponification. The soap is acidified and the liberated resinoid substance is purified. Cadoret named the product "resoline." In general, drying oils give a vigorous reaction with nitric acid, and semi- or non-drying oils do not. Castor and cedar-nut oils are exceptions to this generalization.<sup>80</sup> With fish oil considerable heat is evolved, but the reaction is not especially violent.

Substitutes for India rubber have been made by heating a solution of amber resin in castor oil with sulphur at 180°C., then cooling the mass and ozonizing.

<sup>67</sup> J. H. Harris, U. S. P. 1,249,566, Sept. 18, 1917; *Chem. Abs.*, 1917, 11, 3180.

<sup>68</sup> J. W. Harris, U. S. P. 1,240,567, Sept. 18, 1917; *Chem. Abs.*, 1917, 11, 3180.

<sup>69</sup> H. L. Brownback, French P. 740,913, 1932; *Chem. Abs.*, 1933, 27, 2773.

<sup>70</sup> R. R. Grant, U. S. P. 1,906,749, May 2, 1933, to Blue Rock Chem. Corp. of Va.; *Brit. Chem. Abs. B*, 1934, 1211.

<sup>71</sup> L. E. Gontard, French P. 760,783, 1934; *Chem. Abs.*, 1934, 28, 4260.

<sup>72</sup> German P. 559,848, 1930, to Firma L. Blumer; *Chem. Abs.*, 1933, 27, 878. M. G. Thomson, A. C. Hetherington, S. A. Sim, British P. 403,648, 1932, to Imperial Chem. Ind., Ltd.; *Brit. Chem. Abs. B*, 1934, 209.

<sup>73</sup> J. Scheiber, German P. 555,496, 1929; *Chem. Abs.*, 1932, 26, 5223.

<sup>74</sup> British P. 354,783, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 3916. See also A. Eibner and E. Münsing, *Chem. Umschau*, 1925, 32, 183, 166; *Chem. Abs.*, 1925, 19, 3027.

<sup>75</sup> S. A. Fokin, *J. Russ. Phys.-Chem. Soc.*, 1913, 45, 235; *J.C.S.*, 1913, 104 (1), 442.

<sup>76</sup> M. Morgan, British P. 349,684, 1930; *Brit. Chem. Abs. B*, 1931, 728.

<sup>77</sup> W. F. Reid, *J.S.C.I.*, 1899, 18, 972T.

<sup>78</sup> C. H. Keck, U. S. P. 1,651,459, Dec. 6, 1927; *Chem. Abs.*, 1928, 22, 870.

<sup>79</sup> E. Cadoret, British P. 12,451, 1896; *J.S.C.I.*, 1897, 16, 449.

<sup>80</sup> A. S. Koss, *Przemysl Chem.*, 1920, 4, 161; *Chem. Abs.*, 1923, 17, 3618.

After this the product was treated with sulphur chloride in the presence of benzene and calcium carbonate.<sup>51</sup>

Under the influence of heat, light or proper catalysts (boric acid, stannic chloride or piperidine) ricinoleic acid was found to condense with itself to form diricinoleic acid.<sup>52</sup> This is a thick, yellowish oil, soluble in alcohol, ether, benzene and acetic acid, and reacts with sulphuric acid to yield an unsaturated ester.

#### DISTILLATION OF CASTOR OIL AND DERIVATIVES

Panyutin,<sup>53</sup> in distilling the methyl ester of ricinoleic acid over pumice and borax (in order to prevent polymerization) found that a cleavage in the molecule took place. Heptaldehyde and the methyl ester of undecylic acid ( $\text{CH}_3(\text{CH}_2)_9\text{COOCH}_3$ ) were obtained. No evidence was available for the shifting of the double bond preliminary to the rupture.

Distillation of castor oil in a vacuum or in a stream of inert gas also yields cleavage products, viz., heptaldehyde and undecylenic acid ( $\text{CH}_2=\text{CH}(\text{CH}_2)_9\text{COOH}$ ). The residue is an oil which may be used to make baking lacquers for metals when mixed with unsaturated acids (oleic) together with metal oxides or soaps and plasticizers (benzyl citrate or phthalate). Inasmuch as copper articles are directly oxidized under these conditions, the metal oxide in this instance is omitted.<sup>54</sup> The free acids of castor oil, however, behave differently in that a cleavage does not take place at the carbon containing the hydroxyl group.

According to Heiduschka and Kirsten<sup>55</sup> the distillation of ricinoleic acid yields a product (b.p. 233-4°C. at 14 mm.) which has a percentage composition indicative of the formula  $\text{C}_{18}\text{H}_{32}\text{O}_8$  but which is a mixture and not a single compound.

When the distillation of ricinoleic or elaidoricinoleic acid is carried out in a vacuum, 70-80 per cent distils over as octadecadienoic acid. By combining the distillate and the residue and esterifying with glycerol, Scheiber<sup>56</sup> obtained a product similar to boiled wood oil.

Esterification of the distillation residues of ricinoleic acid with polyhydroxy alcohols has been used by Scheiber for the preparation of lacs<sup>57</sup> wherein oils and resins are also incorporated. They may be used as vehicles for odorless printing inks<sup>58</sup> in which cellulose esters or ethers are added.<sup>59</sup>

The spongy residue left on distillation of castor oil has been found by Barbot<sup>60</sup> to contain a variety of fatty acids. Esterification with ethyl alcohol gave the heptoate, nonate, undecoate, palmitate, ricinoleate, oleate, stearate and 74 per cent of an unknown acid of molecular weight approximately 700, which appears to be formed from the auto-condensation of linoleic acid.

Böeseken and Hoevers<sup>61</sup> investigated the dehydration product of ricinoleic acid by forming adducts of maleic anhydride<sup>62</sup> and determined that 75 per cent was linoleic acid and 15 per cent 9,12-octadecadienoic-1-acid.

<sup>51</sup> H. Tiehsen, *British P.* 17,579, 1904; *J.S.C.I.*, 1904, 23, 1154. H. Spatz, *U. S. P.* 786,527, Apr. 4, 1904; *J.S.C.I.*, 1905, 24, 507. H. Spatz and H. Tiehsen, *German P.* 160,120, 1904. H. Tiehsen, *French P.* 346,349, 1904; *J.S.C.I.*, 1905, 24, 143. Other rubber substitutes containing fatty oils are discussed by J. Lewkowitsch, "Chemical Technology of Oils, Fats and Waxes," Macmillan & Co., Ltd., London, 1915, 191.

<sup>52</sup> A. Zlatarov and V. Bieliavski, *Ann. univ. Sofia, Faculte phys.-math.*, 1932, 28 (2), 21, 39.

<sup>53</sup> P. S. Panyutin, *J. Russ. Phys.-Chem. Soc.*, 1928, 60, 1; *Chem. Abs.*, 1928, 22, 3392.

<sup>54</sup> A. J. Ducampe and M. E. A. Baule, *British P.* 383,856, 1932; *Chem. Abs.*, 1933, 27, 4427.

<sup>55</sup> A. Heiduschka and G. Kirsten, *Pharm. Leutthalde*, 1930, 71, 81; *Chem. Abs.*, 1930, 24, 1933.

<sup>56</sup> J. Scheiber, *British P.* 316,538, 1929; *Brit. Chem. Abs. B.*, 1930, 827. See Chapter 43.

<sup>57</sup> J. Scheiber, *German P.* 512,822 and 512,895, 1931; *Chem. Abs.*, 1931, 25, 1400.

<sup>58</sup> J. Scheiber, *German P.* 522,486, 1928; *Chem. Abs.*, 1931, 25, 3184.

<sup>59</sup> J. Scheiber, *German P.* 544,697, 1930; *Chem. Abs.*, 1932, 26, 3686.

<sup>60</sup> A. Barbot, *Compt. rend.*, 1933, 197, 65; *Brit. Chem. Abs. A.*, 1933, 935.

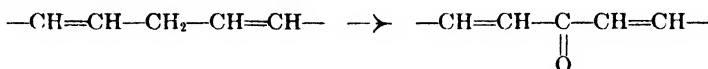
<sup>61</sup> J. Böeseken and R. Hoevers, *Rec. trav. chim.*, 1930, 49, 1165; *Brit. Chem. Abs. A.*, 1931, 198.

<sup>62</sup> See Chapter 40, Diene Synthesis.



## CONVERSION OF NON-DRYING TO DRYING OILS

Scheiber<sup>96</sup> has classified the fatty oils into (1) those containing conjugated double bonds (tung oil) and (2) those containing several double bonds, non-conjugated (linseed and semi-drying oils). Inasmuch as drying is partially the result of the polymerization of the double bonds, tung oil requires but little outside influence. With other oils it is first necessary to oxidize the methylene group between the two double bonds



before a conjugated system results. By shifting the double bonds of the semi-drying oils, however, compounds are obtained which resemble tung oil in drying properties.<sup>97</sup> By treating the fatty oils of the linseed, poppy seed and train oil types at 200°C. with air or carbon dioxide, this shift in the double bonds takes place and a product similar to tung oil is obtained.<sup>98</sup> Other catalysts include sulphuric acid, antimony pentachloride, aluminum oxide and mercuric oxide.<sup>99</sup>

Linseed oil may also be isomerized to yield a system of conjugated double bonds by treatment with chlorine until the chlorine content is about 20-25 per cent and then dehalogenated with a metal. A clear liquid results which may be used for paint.<sup>97</sup> Gardner<sup>98</sup> has applied this same method to obtain a drying oil from soyabean oil glyceride. Addition of 0.03 per cent of cobalt in the form of a drier to dehydrated ricinoleic acid glycerol ester yields a clear film in 3 to 4 hours.<sup>99</sup>

Synthetic drying oils are also formed by heating castor oil with glycerol and subsequent esterification with unsaturated fat or resin acids.<sup>100</sup> Hydroxylated fats may be prepared artificially by chlorinating fish oils and hydrolyzing the resulting products.<sup>101</sup>

The dehydration product of castor oil obtained by vacuum and chemical dehydration may be heated with excess glycerol to form the glyceryl ester of 9,11-octadecadienoic-1-acid. The films of linseed, and tung oil<sup>102</sup> and the triglyceride of 9,11-octadecadienoic-1-acid, containing cobalt and lead-manganese driers, did not yellow within two years in a desiccator but did so within a few months in ordinary air. The coloration is ascribed to oxidation promoted by water as a carrier. The subsequent bleaching in strong light appears to be a reduction process.<sup>103</sup>

## POLYMERIZED PRODUCTS FROM OTHER FATTY OILS

The first stage<sup>104</sup> in the hardening of a film of linseed oil or similar unsaturated fatty oil in the presence of air is the absorption of oxygen by the fatty acid mole-

<sup>96</sup> J. Scheiber, *Farbe u. Lack*, 1930, 51, 63; *Chem. Abs.*, 1930, 24, 2314. For the classification of fatty oils on the basis of drying properties see the International Critical Tables, McGraw-Hill Book Co., Inc., New York, 1927, II, 201.

<sup>97</sup> See J. Scheiber, *Z. angew. Chem.*, 1933, 46, 643; *Brit. Chem. Abs. B*, 1934, 26.

<sup>98</sup> J. Scheiber, U. S. P. 1,896,467, Feb. 7, 1933; *Chem. Abs.*, 1933, 27, 2833. British P. 316,872, 1928; *Chem. Abs.*, 1930, 24, 2315. French P. 678,415, 1929; *Chem. Abs.*, 1930, 24, 1753.

<sup>99</sup> J. Scheiber, British P. 338,932, 1929; *Chem. Abs.*, 1931, 25, 2580.

<sup>97</sup> J. Scheiber, German P. 520,955, 1928; *Chem. Abs.*, 1931, 25, 3502. British P. 316,872, 1928; *Chem. Abs.*, 1930, 24, 2315.

<sup>98</sup> H. A. Gardner, U. S. P. 1,452,553, Apr. 24, 1923; *Chem. Abs.*, 1923, 17, 2197.

<sup>99</sup> G. G. Sward, *Circ. Amer. Paint, Varnish Mfrs. Assoc.*, 1931, 377, 126.

<sup>100</sup> K. Ott and B. Breyer, German P. 572,359, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 27, 3627.

<sup>101</sup> C. Stiepel, British P. 272,198, 1926; *Chem. Abs.*, 1928, 22, 1698.

<sup>102</sup> J. Scheiber, U. S. P. 1,942,775, Jan. 9, 1934; *Chem. Abs.*, 1934, 28, 1879. See J. Scheiber, British P. 306,462, 1928; *Chem. Abs.*, 1929, 23, 5061.

<sup>103</sup> J. Scheiber, *Farbe und Lack*, 1931, 511; *Chem. Abs.*, 1932, 26, 3684.

<sup>104</sup> J. S. Long, A. E. Rheineck and G. L. Ball, Jr., *Ind. Eng. Chem.*, 1933, 25, 1086.

cule in sufficient quantity to provide one peroxide grouping for each ethylenic linkage. When the molecules have grown to a certain degree of complexity or polarity, they associate and form a solid gel. Further oxidation now becomes unimportant, as the polar liquid phase gradually undergoes transition into a solid phase of substantially the same ultimate analysis. Small amounts of ozone accelerate the rate at which these changes occur.<sup>106</sup>

In the preparation of stand oils from linseed and perilla oils, it was found that the gelatinization was a result of the gradual increase in the proportion of polymerized molecules. These are soluble in the remainder of the oil to a limited extent, and when this limit is exceeded they separate in the form of a gel, and cause the whole mass to set.<sup>106</sup> Similarly, the gelation of tung oil is the result of a gradual polymerization.<sup>107</sup> It is true that large amounts of oxygen introduced into linseed oil will cause complete solidification, but the product in this case is a somewhat soluble oxygenated substance, rather than a relatively insoluble polymer.<sup>108</sup> Extraction of oxidized linseed oil with petroleum ether removes the most soluble constituent, namely the unreacted linseed oil.<sup>109</sup> The soluble portion is found to be in the unimolecular state, while the insoluble material is definitely colloidal.<sup>110</sup> Rapid polymerization of linseed oil in the presence of oxygen is said to lead to the formation of undesired hydrophilic compounds. These can be avoided by the use of stand oils prepared in the absence of air.<sup>111</sup>

An interesting study of the role of oxygen in the polymerization of oils was reported by Scheiber.<sup>112</sup> He noted a superiority in the film-forming properties of oils containing conjugated double bonds. The rate of drying of tung oil, which contains a conjugated system, is not markedly decreased by the addition of anti-oxidants. He therefore reasoned that the autoxidation of linseed oil is accompanied by a rearrangement of double bonds to form a conjugated system. The effect is absent when oxygen is excluded, but the amount required is very small, and its influence is definitely catalytic.<sup>113</sup>

While these polymerizations usually occur in the presence of oxygen, by certain special procedures they may be carried out in the atmosphere of an inert gas. A novel method for the thickening of fatty and mineral oils is the "voltolization" process, which consists in subjecting the oil to the effects of an electric glow discharge of about 4000 v. at 500 cycles.<sup>114</sup> The voltage and frequency may be varied within rather wide limits.

Vehicles for lacquers and paints may be obtained by heating drying oils until they reach an iodine number<sup>115</sup> of 110 to 95 and treating the product with a hot alcoholic or ester solvent. Upon cooling the solution, an oil useful for lacquers and paints separates. Linseed oil, for example, which has been heated at 300°C. in the absence of air, is stirred with malonic ester.<sup>116</sup> This treatment extracts the

<sup>106</sup> C. Denzler, *Helv. Chim. Acta*, 1933, 16, 807; *Chem. Abs.*, 1933, 27, 4696.

<sup>107</sup> A. Steger and J. van Loon, *Rec. trav. chim.*, 1934, 53, 769; *Chem. Abs.*, 1934, 28, 5259.

<sup>108</sup> F. T. Walker, *J.S.C.I.*, 1934, 53, 104. A. Steger and J. van Loon, *Rec. trav. chim.*, 1934, 53, 860; *Brit. Chem. Abs. B*, 1934, 847.

<sup>109</sup> H. Ender, German P. 599,841, 1934; *Chem. Abs.*, 1934, 28, 7562.

<sup>110</sup> W. S. Egge and R. D. Bounney, U. S. P. 1,968,244, July 31, 1934, to Congoleum-Nairn, Inc.; *Chem. Abs.*, 1934, 28, 6003.

<sup>111</sup> K. Lins, *Z. angew. Chem.*, 1934, 47, 564; *Chem. Abs.*, 1934, 28, 6578.

<sup>112</sup> F. Ohl, *Farbe u. Lack*, 1934, 363; *Chem. Abs.*, 1934, 28, 6325. J. Scheiber, *Z. angew. Chem.*, 1933, 46, 643; *Brit. Chem. Abs. B*, 1934, 26.

<sup>113</sup> J. Scheiber, *Farbe u. Lack*, 1934, 326, 339; *Brit. Chem. Abs. B*, 1934, 803.

<sup>114</sup> It has been reported that  $\beta$ -naphthol causes an actual acceleration of the drying rate of tung oil. C. A. Thomas and P. E. Marling, *Ind. Eng. Chem.*, 1932, 24, 871.

<sup>115</sup> E. C. Isom, *Oil and Gas J.*, 1926, 24, 156; *Chem. Abs.*, 1926, 20, 281. For a more detailed discussion of voltolized oils see Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., New York, 1934, Chap. 9. See also A. W. Nash, J. L. Howard and F. C. Hall, *J. Inst. Pet. Tech.*, 1934, 20, 1027.

<sup>116</sup> See Vaubel, *Farben-Ztg.*, 1932, 37, 1482; *Chem. Abs.*, 1932, 26, 5437 (use of bromine numbers for controlling cooking of oils).

<sup>117</sup> A. Eibner and M. Miller, German P. 546,679, 1929; *Chem. Abs.*, 1932, 26, 3685. See also A. Eibner,

unpolymerized portion of the oil. Media for oil varnishes and enamels, which have been given the trade name, "Tekaoils," consist of linseed stand oils from which the low-polymerized, highly dispersed portion has been removed. They do not oxidize on exposure, but polymerization is pronounced. Tekaoil films dry more rapidly than stand-oil films and are more durable; also, it is said that zinc white and titanium white settle much less rapidly in Tekaoils than in stand oils of the same viscosity. "Olovine" varnish is prepared by heating Tekaoil with a polyvinyl ester (acetate).<sup>117</sup> Olovine in butyl acetate can be used in conjunction with nitrocellulose.<sup>118</sup> Heating linseed oil at about 300°C. until an iodine value of approximately 180 is reached, followed by air-blowing, results in products for paints and varnishes.<sup>119</sup> Mixtures of castor and linseed oils may be treated in the same manner at 75-150°C.

A molecular still which has been suggested<sup>120</sup> for the separation of constituents of polymerized drying oil consists of concentric tubes placed close together. The oil is caused to evaporate from the inner tube, which is heated, to the outer tube, which is cooled. The process is carried out at a pressure as low as the vacuum of a cathode tube.

Auer<sup>121</sup> noted that "isocolloid" materials containing unsaturated high-molecular fatty acids undergo a physical or physico-chemical change on heating with so-called "electrolytes" (salts, metallic organic derivatives and lower organic acids). The effect is to convert liquid materials into solids, or, conversely, to develop thin or pasty liquids from resinous substances. A variety of glyceride oils may be so modified, e.g., castor, olive, sunflower, tung, linseed and fish oils, by treatment with 2-10 per cent of a wide range of reagents.<sup>122</sup> Included are inorganic substances, e.g., silica gel, fuller's earth, sodium bisulphite and a considerably longer list of organic substances, e.g., formaldehyde, phenol,  $\alpha$ -naphthol, pyrogallol, thiocarbonyl, benzidine, 2,3-hydroxynaphthoic acid, benzene and glycerol. Use of an electric current during heating aids in bringing about modification.

Water-insoluble "modifiers" are used to prepare waterproof varnish bases, and gas-generating materials (carbonates, sulphites) are utilized for production of rubber substitutes.<sup>123</sup>

Substances applicable for the manufacture of soaps, varnishes and linoleum are secured by heating unsaturated fatty acids with peroxides, oxides or hydroxides of alkali metals.<sup>124</sup> Products of desired solubility and viscosity are obtained by addition of o-nitro phenol, p-cresol or benzoic acid.<sup>125</sup>

By oxidizing oils containing glycerides of unsaturated acids, and condensing the product with a polyhydric alcohol, condensation products are formed.<sup>126</sup> Treatment of a mixture of linseed and tung oils with zinc oxide and adding sufficient

U. S. P. 1,870,614, Aug. 9, 1932; *Chem. Abs.*, 1932, 26, 5777. German P. 548,152, 1930 and 567,133, 1929; *Chem. Abs.*, 1932, 26, 4190; 1933, 27, 1529. British P. 370,614, 1931; *Brit. Chem. Abs. B.*, 1932, 612. French P. 708,465, 1930; *Chem. Abs.*, 1932, 26, 1142. See also T. Kothhoff, German P. 575,789, 1933, 583,221, 1933 and 598,725, 1934; *Chem. Abs.*, 1933, 27, 4942; 1934, 28, 2554, 6002.

<sup>117</sup> See Chapter 51.

<sup>118</sup> T. H. Barry and L. Light, *Brit. Plastics*, 1932, 3, 28; *Brit. Chem. Abs. B.*, 1932, 806.

<sup>119</sup> A. Schwarzman, U. S. P. 1,958,372 to 1,958,374, May 8, 1934, to Spencer Kellogg & Sons, Inc.; *Chem. Abs.*, 1934, 28, 4255.

<sup>120</sup> French P. 765,839, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 7042.

<sup>121</sup> L. Auer, British P. 287,943, 1926; *Brit. Chem. Abs. B.*, 1928, 398. French P. 632,796, 1926; *Chem. Abs.*, 1929, 23, 3805. Swiss P. 130,435, 1926; *Chem. Abs.*, 1929, 23, 3713. Also L. Auer, *Chem. Umschau* *Fette, Oleo Wachse, Harze*, 1928, 35, 9, 27; *Chem. Abs.*, 1928, 22, 1695.

<sup>122</sup> L. Auer, British P. 321,689, 1929; *Brit. Chem. Abs. B.*, 1930, 652. See also Hungarian P. 104,941, 1933; *Chem. Abs.*, 1933, 27, 4133.

<sup>123</sup> L. Auer, British P. 321,724 to 321,727, 1929; *Brit. Chem. Abs. B.*, 1930, 652.

<sup>124</sup> L. Auer, U. S. P. 1,980,366, Nov. 13, 1934, to J. R. Newman; *Chem. Abs.*, 1935, 29, 254. British P. 321,690, 321,723 and 321,723, 1928; *Brit. Chem. Abs. B.*, 1930, 67; *Chem. Abs.*, 1930, 24, 2918, 2911. French P. 674,703, 1929; *Chem. Abs.*, 1930, 24, 2846. See also British P. 341,453, 1929; *Brit. Chem. Abs. B.*, 1931, 450. Also L. Auer and L. Sustek, U. S. P. 1,963,068, June 19, 1934; *Chem. Abs.*, 1934, 28, 4924.

<sup>125</sup> L. Auer, British P. 337,736, 1929; *Chem. Abs.*, 1931, 25, 2311.

<sup>126</sup> German P. 695,669, 1934, to Degussa A.-G.; *Chem. Abs.*, 1934, 28, 5263

benzoic or cinnamic acid to combine with all the zinc yields lustrous plastic masses.<sup>127</sup> Poppyseed or other drying oils may replace the linseed or tung oil.<sup>128</sup> For use in printing inks and artists colors, the addition of hexamethylenetetramine is recommended.<sup>129</sup>

A number of catalysts other than oxygen or alkaline materials have been used to assist the polymerization of drying oils. Finely divided metals, platinum, copper, palladium, iron, nickel or cobalt, accomplish the result at elevated temperatures.<sup>130</sup> Unsaturated oils heated at 250-300°C., in the presence of sulphur dioxide, hydrogen sulphide, carbon dioxide or hydrogen, under a reduced pressure of 15 to 145 mm., give polymerized oils,<sup>131</sup> which, when heated with a soap and vulcanized, are converted into rubber substitutes. These, in turn, are incorporated with solvents, fillers, cellulose esters and plasticizers to serve as varnishes.

Diolefins are also said to be polymerizable in mixture with glyceride oils (linseed, tung, castor or train oil) in the presence of aluminum chloride at ordinary or higher temperatures. The rubber-like product is extracted with solvents.<sup>132</sup>

Ott and Schüssler<sup>133</sup> treated unsaturated fatty acids or their esters or amides simultaneously with a sulphite and an oxidizing agent without the addition of acid. Compounds of cobalt, lead, manganese or iron may be added. Thus linseed oil heated at 100°C. for 16 hours with a 38 per cent solution of sodium bisulphite in the presence of air and lead-manganese naphthenate gave products soluble in water, and useful for dressing natural or artificial silk, and as wetting or greasing agents.

Stubner<sup>134</sup> employed an unsaturated fatty acid derived from tung oil (or from linseed oil) as a solvent for shellac or other gums, obtaining in this way a plastic insulating material, suitable for covering cables.

Reactions between fatty acids and various amino compounds have yielded substances useful in shoe polishes, floor dressings and similar products. Thus, p-aminophenol and oleic acid combine to form a black, waxy substance, soluble in most organic solvents.<sup>135</sup> Linseed oil or tung oil heated at 200-250°C. with 2 to 10 per cent of a primary aromatic amine yields a product which may be vulcanized, and finds use in varnishes and in rubber substitute manufacture.<sup>136</sup> Phenols may be condensed with the higher unsaturated fatty acids or glycerides in the presence of sulphuric acid.<sup>137</sup>

Treating linseed oil so that it dries essentially by the evaporation of a stabilizing solvent, ethanol, results in a product which can be incorporated in nitrocellulose lacquers to eliminate many of the weaknesses of ordinary blown or heat-treated oils.<sup>138</sup> Halovinyl compounds, vinyl acetylene<sup>139</sup> or vinyl naphthylene, in combination

<sup>127</sup> A. Rogler, German P. 445,799, 1925; *Brit. Chem. Abs.* B, 1929, 138. See also German P. 491,728, 1927; *Chem. Abs.*, 1930, 24, 2558.

<sup>128</sup> A. Rogler, German P. 549,762, 1928; *Chem. Abs.*, 1932, 26, 4925.

<sup>129</sup> H. Vollmann, German P. 568,693, 1927; *Chem. Abs.*, 1933, 27, 2829.

<sup>130</sup> British P. 366,620, 1929, to Oelwerke Noury & van der Lande, G. m. b. H.; *Chem. Abs.*, 1933, 27, 2050.

<sup>131</sup> H. M. Bunbury, British P. 343,099, 1929, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1931, 25, 4428. German P. 582,287, 1933; *Chem. Abs.*, 1933, 27, 5217. German P. 600,647, 1934; *Chem. Abs.*, 1934, 28, 7594.

<sup>132</sup> H. Plauson, German P. 361,429, 1917; *J.S.C.I.*, 1923, 42, 366A.

<sup>133</sup> K. Ott and H. Schüssler, German P. 551,424, 1930, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4494. See also British P. 402,759, 1932, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1934, 209.

<sup>134</sup> E. de Stubner, U. S. P. 1,494,063, May 13, 1924; *Chem. Abs.*, 1924, 18, 2258.

<sup>135</sup> Carleton Ellis, U. S. P. 1,475,477, Nov. 27, 1923; *Chem. Abs.*, 1924, 18, 761.

<sup>136</sup> L. Auer, British P. 337,732, 1929; *Chem. Abs.*, 1931, 25, 2312. See also A. Bowles, *Paint, Oil, Chem. Rev.*, 1928, 86, 10; *Chem. Abs.*, 1929, 23, 1291.

<sup>137</sup> British P. 310,562, 1928, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs.* B, 1929, 636. See Chapter 19.

<sup>138</sup> S. R. Grovenstein and G. F. Beal, *Official Digest Fed. Paint Varnish Prod. Clubs*, 1933, 125, 137; *Chem. Abs.*, 1933, 27, 4105. T. H. Barry and L. Light, *Paint, Varnish Prod. Mgr.*, 1933, 9 (10), 30.

<sup>139</sup> See Chapter 8.

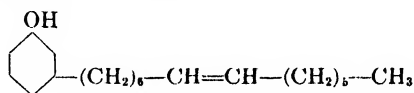
with stand oils, give polymerized products<sup>140</sup> from which lacquers can be manufactured.

Paints and leather preservatives based on the treatment of linseed oil with a solution of chromyl chloride followed by the removal of the latter by distillation *in vacuo*, are stated<sup>141</sup> to be unsatisfactory. Other chlorides which have been used with linseed oil to produce vehicles for paints are titanium tetrachloride and silicon tetrachloride.<sup>142</sup>

The unsaturated fatty acids from Japanese sardine oil are polymerized by heating at 240-320°C., with the formation of resinous substances. Evidence suggests that an extramolecular polymerization is preceded by some type of intramolecular change such as ring formation.<sup>143</sup>

#### CASHEW-SHELL OIL RESINS

The oil extracted from the shell of the cashew nut contains anacardic acid ( $\text{HO}-\text{C}_{21}\text{H}_{37}-\text{COOH}$ ) and cardol ( $\text{C}_{32}\text{H}_{52}\text{O}_4$ ) which is probably a phenolic compound.<sup>144</sup> The commercial fluid is heat-treated, a process which destroys the anacardic acid. The chief constituent of the heated liquid has been named cardanol and assigned, tentatively, the formula



Formerly the oil was a waste product, but Harvey<sup>145</sup> has developed its use as a raw material for the manufacture of varnishes and impregnating materials known as "Harvel," "Oil Stop" and "Cardolite," and it now has a considerable commercial significance.

The principal source of crude cashew-shell fluid is India, but Portuguese East Africa, Cuba, Guatemala and Brazil are potential suppliers. The raw oil has a high iodine value (270-290), but despite this it is non-drying. This may be due to the anti-catalytic action of the phenolic constituents.<sup>146</sup> The iodine value of the commercial fluid is about 260. Although thin films of the oil remain unchanged when exposed to air for some time, oxygen absorption occurs rapidly once it has been initiated.<sup>147</sup>

The application of the oil is based on two important characteristics. It polymerizes on heating at 100-200°C. with an acid or alkaline catalyst; and it forms condensation products with aldehydes, probably because of its phenolic components. Harvey's view of the polymerization of cashew fluid in the presence of sulphuric acid postulates addition of the latter to the double bond of cardanol and subsequent elimination of sulphuric acid between two molecules as follows:

<sup>140</sup> O. Jordan, H. Hopff and E. Kühn, *German P.* 580,234, 1933 and 588,306, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 4943; 1934, 28, 1558.

<sup>141</sup> R. Kuhn, *Chem.-Ztg.*, 1924, 48, 942; *J.S.C.I.*, 1925, 44, 106B.

<sup>142</sup> M. Tencer, *German P.* 597,266, 1934, to Przetwornia Olejow Roslinnych Spolka Akcyjna; *Chem. Abs.*, 1934, 28, 5261.

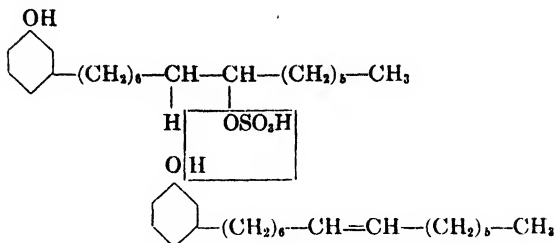
<sup>143</sup> I. Y. Toyama and T. Tsuchiya, *Chem. Umschau*, 1929, 36, 45; *Brit. Chem. Abs. B.*, 1929, 291. *Bull. Tokyo Inst. Ind. Research*, 1928, 23 (5), 15; *Chem. Abs.*, 1929, 23, 1873.

<sup>144</sup> S. Ruhemann and S. Skinner, *Ber.*, 1887, 20, 1861. I. Joseph and J. J. Sudborough, *J. Ind. Inst. Sci.*, 1923, 5, 133; *Chem. Abs.*, 1923, 17, 1897.

<sup>145</sup> M. T. Harvey, U. S. P. 1,725,791 to 1,725,797, Aug. 27, 1929, to Harvel Corp.; *Chem. Abs.*, 1929, 23, 5051. *German P.* 533,870 and 563,646, 1928; *Chem. Abs.*, 1932, 26, 861; 1933, 27, 1217. *British P.* 283,803, 1926; *Brit. Chem. Abs. B.*, 1928, 237. See also C. E. Peczenik and F. Schamberger, *British P.* 283,233; *Brit. Chem. Abs. B.*, 1928, 275.

<sup>146</sup> H. A. Gardner, *Circ., U. S. Paint Mfrs. Assoc.*, 1923, 180, 241; *Chem. Abs.*, 1923, 17, 2512.

<sup>147</sup> M. T. Harvey, *loc. cit.*



If equal volumes of the oil and 40 per cent formalin are heated at 100-200°C. with 16 per cent of the total volume of hydrochloric acid, a liquid is formed which can be separated and heated at 80-140°C. under pressure to give a hard, molded body. In another method, a compact article is produced by impregnating layers of textile material with a varnish made from the formaldehyde-cashew fluid condensate. For this purpose, the varnish may include 25-35.5 per cent tung oil and 12.5-25 per cent rosin.<sup>148</sup>

Prior to the preparation of a molding composition, the cashew-shell liquid may be heated to about 300°C. and then cooled to room temperature. A mixture of the treated oil with 0.1 of its weight of paraform and about 0.9 of its weight of wood flour is molded and then cured at 140°C. for 5 hours. Instead of molding this composition, it may be employed with paper in the preparation of rolled laminated tubing, which is cured for 16 hours at 140°C. A similar procedure is applicable with hexamethylenetetramine substituted for the paraform. Only about one-third as much tetramine as paraform is required. In the case of hexamethylenetetramine, the reaction product is liquid, and dippings or coatings may be made prior to the cure.<sup>149</sup> For some purposes it is desirable to add pitch or casein to the composition.<sup>150</sup> Hardwood pitch and heat-treated cashew fluid form a petroleum-insoluble composition that can be utilized for coating or impregnating.<sup>151</sup>

A substitute for shellac is obtained by heating cashew-shell oil to 140-200°C. with copper, aluminum or lead or the oxides, hydroxides and carbonates of these metals. A liquid product is separated from the metallic compound, dissolved in alcohol or naphtha and used as a varnish.<sup>152</sup> The liquid material also has drying properties and may be employed for coating and impregnating.<sup>153</sup>

The non-drying characteristic of the oil may be eliminated, as noted above, by heating with metals or metallic compounds, and the rate of drying of the product is found to be controlled by (1) the temperature and time of the reaction and (2) the metal or salt employed. A drier, such as manganese resinate, may be incorporated with the cashew-shell fluid.<sup>154</sup> Copper can be coated with an insoluble insulating material by covering it with heat-modified cashew-shell liquid (drying oils and resins may be included) through the medium of a varnish solvent. Formaldehyde, hexamethylenetetramine or urea can be added to assist in the setting of the coat.<sup>155</sup> Cashew-shell oil, when heated and air-blown in the presence

<sup>148</sup> A. I. Abrahams, British P. 401,474, 1933; *Chem. Abs.*, 1934, 28, 2864.

<sup>149</sup> M. T. Harvey, U. S. P. 1,921,292, Aug. 8, 1933, to Harvel Corp.; *Chem. Abs.*, 1933, 27, 5203.

E. D. Crammond and W. A. Hughes, U. S. P. 1,921,309, Aug. 8, 1933; *Chem. Abs.*, 1933, 27, 4961.

<sup>150</sup> M. T. Harvey, U. S. P. 1,952,313, March 27, 1934, to Harvel Corp.; *Chem. Abs.*, 1934, 28, 8541.

<sup>151</sup> F. M. Damits, U. S. P. 1,912,435, June 6, 1933, to Harvel Corp.; *Chem. Abs.*, 1933, 27, 4865.

<sup>152</sup> M. T. Harvey, U. S. P. 1,725,793, Aug. 27, 1929, to Harvel Corp.; *Chem. Abs.*, 1929, 23, 5051.

British P. 272,510; *Brit. Chem. Abs.* B, 1929, 902.

<sup>153</sup> M. T. Harvey, U. S. P. 1,725,794 and 1,725,795, Aug. 27, 1929, to Harvel Corp.; *Chem. Abs.*, 1929, 23, 5051. U. S. P. 1,838,073, Dec. 22, 1931; *Brit. Chem. Abs.* B, 1932, 894. British P. 275,574, 1927; *Brit. Chem. Abs.* B, 1929, 179.

<sup>154</sup> M. T. Harvey, U. S. P. 1,735,797, Aug. 27, 1929, to Harvel Corp.; *Chem. Abs.*, 1929, 23, 5051. See also V. A. Ryan, U. S. P. 1,838,072, Dec. 22, 1931, to Harvel Corp.; *Brit. Chem. Abs.* B, 1932, 900.

<sup>155</sup> M. T. Harvey, U. S. P. 1,838,077, Dec. 22, 1931, to Harvel Corp.; *Brit. Chem. Abs.* B, 1932, 900.

<sup>156</sup> M. T. Harvey, U. S. P. 1,821,095, Sept. 7, 1931 and 1,939,301, Dec. 12, 1933, to Harvel Corp.; *Chem. Abs.*, 1931, 25, 5959; *Brit. Chem. Abs.* B, 1934, 1067.

of copper, lead, manganese, lead oxide, copper carbonate or copper oleate, combines with aldehydes to give resins that find use in varnishes. Materials including waxes and resins are added to vary the characteristics of the product.<sup>156</sup> A water-proofing composition for walls was reported to have been secured by treating cashew-shell oil with sufficient alkaline material (barium hydroxide, cement) to react with free acid and glycerides.<sup>157</sup>

The action of nitric acid on cashew fluid converts the latter into a quick-drying coating material which is soluble in amyl acetate, turpentine or alcohol.<sup>158</sup> To carry out this reaction, 1 part by volume of cashew-shell oil, 1 part of nitric acid (sp. gr. 1.42) and 1 part of water are mixed. The reaction is strongly exothermic and is complete in a few minutes. The resinous product formed has an iodine value of zero.<sup>159</sup>

Artificial rubber compositions are formed when cashew fluid is heated with glycerol at 240°C. The products may be vulcanized with sulphur, giving an



*Courtesy Louisville Drying Machinery Co.*

FIG. 166.—Air Dryer for Plastic Materials.

elastic material soluble in the usual rubber solvents.<sup>160</sup> A composition applicable in electrical insulation is prepared by mixing rubber with vulcanized cashew-shell oil and continuing the vulcanization.<sup>161</sup> Cashew-shell oil has been proposed also as a plasticizer for cellulose products, sulphur, resins, rubber and waxes.<sup>162</sup> Tung oil containing 25 per cent of cashew-shell liquid may be heated to 315°C. without risk of gelation, yielding a varnish base with copper oleate. The shell liquid can also be employed to reclaim overheated gelled tung oil,<sup>163</sup> for it redisperses the gel, forming compositions utilized as varnish bases.<sup>164</sup> A substance having germicidal properties may be obtained from cashew-shell oil. Thus, Harvey<sup>165</sup> distilled the

<sup>156</sup> M. T. Harvey, British P. 300,654, 1927, to Harvel Corp.; *Chem. Abs.*, 1929, 23, 3998. French P. 635,579, 1927. *Chem. Abs.*, 1928, 22, 4844.

<sup>157</sup> M. T. Harvey, U. S. P. 1,977,826, Oct. 23, 1934, to Harvel Corp.; *Chem. Abs.*, 1935, 29, 258.

<sup>158</sup> M. T. Harvey, U. S. P. 1,725,792, Aug. 27, 1929, to Harvel Corp.; *Chem. Abs.*, 1929, 23, 5051.

<sup>159</sup> M. T. Harvey, Canadian P. 285,183, 1928; *Chem. Abs.*, 1929, 23, 1000. German P. 538,784, 1926; *Chem. Abs.*, 1932, 26, 2334. British P. 259,959, 1926; *Brit. Chem. Abs. B*, 1928, 376.

<sup>160</sup> M. T. Harvey, U. S. P. 1,771,785 and 1,771,786, July 29, 1930, to Harvel Corp.; *Brit. Chem. Abs. B*, 1930, 918; 1931, 307. British P. 262,134, 1926; *Brit. Chem. Abs. B*, 1928, 420. French P. 632,454, 1926; *Chem. Abs.*, 1928, 22, 3552.

<sup>161</sup> M. T. Harvey, U. S. P. 1,819,416, Aug. 18, 1931, to Harvel Corp.; *Chem. Abs.*, 1931, 25, 5720.

<sup>162</sup> M. T. Harvey, U. S. P. 1,838,071, Dec. 22, 1931, to Harvel Corp.; *Brit. Chem. Abs. B*, 1933, 900.

<sup>163</sup> M. T. Harvey, U. S. P. 1,838,076, Dec. 22, 1931, to Harvel Corp.; *Brit. Chem. Abs. B*, 1932, 900.

<sup>164</sup> V. A. Ryan, U. S. P. 1,927,220, Sept. 19, 1933, to Harvel Corp.; *Chem. Abs.*, 1933, 27, 5995.

<sup>165</sup> M. T. Harvey, U. S. P. 1,950,085, Mar. 6, 1934, to Harvel Corp.; *Chem. Abs.*, 1934, 28, 3188.

liquid (b.p. 305-400°C.) and heated the distillate with 0.2 per cent sodium hydroxide at 150°C. After redistillation, the water-soluble portion of the residue (a sodium salt of a high-molecular-weight phenol) serves as a germicide.

A series of coloring materials ranging from deep red to violet can be prepared by the interaction of cashew-shell oil with ammonium hydroxide or carbonate. The colored product is thickened by hydrochloric acid or formaldehyde, and can then be used for coloring oils or dyeing oilcloth.<sup>100</sup>

The importance of cashew-shell fluid is illustrated by the diversity of its applications. Washers for bottles or jars containing foodstuffs, cosmetics, mayonnaise, etc. are prepared by running paper through the cashew-shell liquid and then through a heated tower. Two or more coats are applied in this manner, and the paper is backed with paper-pulp board and punched into disc form. Compositions containing cashew-shell oil are also used to impregnate cloth or paper for electrical insulation, as baking-type varnishes and as acid-resistant paints.

A slowly polymerizing composition is applied in airplane magneto insulation. Cashew fluid is first partially polymerized by treatment with sulphuric acid, giving a thickened oil which hardens spontaneously to a resinous mass on the addition of paraformaldehyde. The time of the spontaneous cure can be regulated by the acidity of the composition. The partially polymerized cashew liquid is mixed with paraform immediately before use and pumped under pressure into the magneto where it is allowed to harden at room temperature. A somewhat similar material is applied as a lining for electrolytic tanks employed in copper and silver refining. Semi-solid masses with additions of asbestos may be troweled upon the surface and allowed to harden. The cure takes place without the application of heat.

One advantage found in the cashew-shell liquids is the oil-resistance of their polymers and formaldehyde reaction products. Oil Stop, a black, viscous liquid developed from cashew oil, is extensively used with paraform in cable splices. The paraform is incorporated with the liquid and coated over a lead splicing-sleeve. Alternate layers of cotton tape and Oil Stop are built up forming an oil-tight, waterproof seal. The seal can be applied to rubber, metal or paper.

Highly polymerized cashew-shell liquid (Cardolite) may be compounded with rubber and is used in typewriter rolls, brake linings and as a protection against corona discharge on rubber insulation. Brake linings can be manufactured by laminating thin sheets of partially hardened rubber with Cardolite and sheets of asbestos. In another method, a composition consisting of partially polymerized Cardolite, rubber cement and asbestos fiber is forced out of an extrusion apparatus.

#### MISCELLANEOUS COMPOSITIONS

Many oils other than those which have just been considered also have polymerizing properties. For instance, Gardner<sup>107</sup> found that the oil from oiticica seeds bodies rapidly on heating, although less rapidly than tung oil. The fatty acids of oiticica oil are more soluble in turpentine, butyl alcohol and ethyl acetate than the acids from tung oil, but less soluble in ethyl alcohol and mineral spirits. The heat-treated oil has been recommended for making linoleum, factice and airplane finishes.<sup>108</sup> The potential use of oiticica oil in varnishes is more or less dependent on its availability. The oil from the seeds of *Sterculia foetida* (Bangor nut) can

<sup>100</sup> M. T. Harvey, British P. 272,509, 1926, to Harvel Corp.; *Chem. Abs.*, 1928, 22, 1862.

<sup>107</sup> H. A. Gardner, *Circ., U. S. Paint Mfrs. Assoc.*, 1923, 177, 220; *Circ., National Paint, Varnish and Lacquer Assoc.*, 1934, 470, 213; *Chem. Abs.*, 1935, 29, 362.

<sup>108</sup> R. Lüde, *Fettechem. Umschau*, 1935, 42, 4; *Chem. Abs.*, 1935, 29, 2002; *Brit. Chem. Abs. B*, 1935, 304.



be heat-treated to form a composition for coating metals.<sup>160</sup> A different type of resinifiable substance is that which was obtained by Lifschutz<sup>170</sup> from the unsaponifiable matter of wool-fat. Loeschigk<sup>171</sup> utilized the foots obtained in refining cottonseed oil and similar products (consisting of soaps, neutral fats, resins and albuminous substances) by oxidizing with peroxide. After the addition of acid the fatty matter is recovered by means of solvents, and the remainder is an amorphous, resinous mass. Cotton oil also finds use in the manufacture of a plastic material for molding accumulator vats.<sup>172</sup> A composition is made which consists of cotton-oil residues (40 per cent), petroleum tar (20 per cent), kieselguhr (30 per cent) and asbestos or jute (10 per cent).

The fatty acids of drying oils can be esterified with quebrachitol, using a solvent and a catalyst, to procure modified products capable of thickening by heat or blowing with air.<sup>173</sup> These are said to be adaptable for paints and varnishes. A coating composition was developed by Albrecht<sup>174</sup> by heating triethanolamine with a fatty acid until esterification was complete, then adding phosphoric acid. An ester-phosphate compound is formed, which is reported to be of value in paints and varnishes for metal, in that it introduces the phosphate in soluble form.

Sandal seed oil thickens to a resinous mass on exposure to light. At 130-140°C., sulphur is absorbed and plastic rubber-like compounds are formed.<sup>175</sup>

A number of resinous materials can be made by treating fatty substances with higher alcohols. Thus, Brosel<sup>176</sup> treated fatty acids and esters with carnaubyl, cetyl or melissyl alcohol in the presence of litharge (which saponified a portion of the fatty acids to form lead soaps which acted as driers) to obtain rubber-like masses which could be dissolved in solvents to form varnishes. The catalytic oxidation of hydrocarbons<sup>177</sup> produces hydroxy acids which can be dehydrated to form unsaturated acids. These, in turn, are esterified with glycerine and may be oxidized to products resembling linoxyn.<sup>178</sup>

A "reinforced" oil<sup>179</sup> is made by heating a vegetable drying oil at 200°C. until it is substantially "deglycerolated," and then treating the residue with a quantity of glycerol in excess of that removed. The mixture is now heated with an acidic resin until the product has the desired degree of clarity and consistency.

Esterification of unsaturated fatty acids with polyvalent phenols (in the presence of zinc or aluminum chloride) yields products resembling oriental lacquers.<sup>180</sup> These compositions can be modified by condensation with formaldehyde.<sup>181</sup> Under the influence of boron fluoride unsaturated fatty acids react with phenols to form viscous compositions which may be drawn into threads.<sup>182</sup> Linseed oil with resorcinol and catalytic quantities of hydrogen chloride gives viscous condensation prod-

<sup>160</sup> M. T. Harvey, U. S. P. 1,939,773, Dec. 19, 1933, to Harvel Corp.; *Chem. Abs.*, 1934, 28, 1557.

<sup>170</sup> I. Lifschutz, U. S. P. 1,252,591, Jan. 8, 1918; *Chem. Abs.*, 1918, 12, 773.

<sup>171</sup> H. Loeschigk, German P. 220,582, 1909; *J.S.C.I.*, 1910, 29, 640.

<sup>172</sup> French P. 692,565, 1930, to Compagnie française d'accumulateurs électriques; *Chem. Abs.*, 1931, 25, 1645.

<sup>173</sup> A. Hill and E. E. Walker, British P. 406,738, 1934, to Imperial Chem. Ind., Ltd.; *Chem. Abs.*, 1934, 28, 4922.

<sup>174</sup> H. O. Albrecht, U. S. P. 1,936,534, Nov. 21, 1933, to E. I. du Pont de Nemours & Co.; *Chem. Abs.*, 1934, 28, 917.

<sup>175</sup> M. Screenivasaya and N. Narayana, *Proc. 15th Indian Sci. Congr.*, 1928, 160; *Chem. Abs.*, 1931, 25, 2868.

<sup>176</sup> F. Brosel, German P. 597,467, 1933, to Vereinigte Farben-und Lackfabriken; *Chem. Abs.*, 1933, 27, 4699.

<sup>177</sup> See Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co., 1934, 971.

<sup>178</sup> M. Luther and H. Beller, U. S. P. 1,901,374, March 14, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 3094.

<sup>179</sup> J. V. Hunn, Canadian P. 334,928, 1933, to Hemingway & Co., Inc.; *Chem. Abs.*, 1933, 27, 5560.

<sup>180</sup> J. Scheiber, German P. 537,339, 1930; *Chem. Abs.*, 1933, 27, 434. French P. 755,422, 1933, to Soc. des laques et matières plastiques; *Chem. Abs.*, 1934, 28, 1557. British P. 415,582, 1933, to Soc. des laques et matières plastiques; *Brit. Chem. Abs. B.*, 1934, 972.

<sup>181</sup> German P. 576,714, 1933, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 352.

<sup>182</sup> French P. 757,841, 1934, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1934, 28, 3196. British P. 401,237, 1933; *Brit. Chem. Abs. B.*, 1934, 454.

ucts of intense red color.<sup>188</sup> For the preparation of sizing materials it is suggested that the linseed oil be sulphonated during condensation with resorcinol.<sup>184</sup>

Ferrous linoleate is soluble in turpentine and in dichlorobenzene, and this solution has been used as the basis of a paint medium.<sup>186</sup> When linseed oil is heated at 180-200°C. with acid sludge or acid resins from the refining of mineral oils it forms linoleum-like plastic masses.<sup>186</sup>

Diesser<sup>187</sup> prepared a resinous body by heating cellulose with fatty oils. Scholz<sup>188</sup> found that a plastic composition is obtained when a mixture of linoxyn (free from solvents) and nitrocellulose (swelled in a volatile solvent such as ethyl acetate) is stirred until homogeneous and then molded under pressure.

Resinous substances are obtained by dissolving old varnish or resin coatings in solutions of sodium or ammonium carbonate or hydroxide, sodium borate, etc., and treating the solution with sodium hypochlorite or free chlorine. The resin is precipitated by sulphuric acid or sulphur dioxide, and the dried precipitate is used in the preparation of varnishes.<sup>189</sup> Horn scrap is reported to be soluble in linseed oil at 300°C., and the solution has been proposed for use as a paint vehicle and as a varnish.<sup>190</sup>

<sup>188</sup> A. Barreto, *Rev. chim. ind. (Rio de Janeiro)*, 1933, 2, 337; *Chem. Abs.*, 1934, 28, 3917.

<sup>184</sup> Swiss P. 166,789, 1934, to Soc. pour l'ind. chim à Bâle; *Chem. Abs.*, 1934, 28, 5611.

<sup>185</sup> German P. 339,574, 1919, to A.-G. für Anilin-Fabr.; *J S C I.*, 1921, 40, 742A. See Chapter 37.

<sup>186</sup> L. Bolgar, U. S. P. 1,842,857, Jan. 26, 1932, to Laslo d'Antal, *Chem. Abs.*, 1932, 26, 1812. German P. 585,766 and 538,800, 1933; *Chem. Abs.*, 1934, 28, 1558.

<sup>187</sup> G. Diesser, British P. 11,166, 1909; *J S C I.*, 1909, 28, 945

<sup>188</sup> V. Scholz, U. S. P. 1,889,702, Nov. 29, 1932, to Atlas Ago Chemische Fabrik A -G; *Chem. Abs.*, 1933, 27, 1724.

<sup>189</sup> C. Littleton, U. S. P. 1,398,438, Nov. 29, 1921; *Chem. Abs.*, 1922, 16, 842.

<sup>190</sup> G. Diesser, *Kunststoffe*, 1924, 14, 46.

## Chapter 62

# Inorganic Resins

Although almost all resinous materials are natural or synthetic carbon compounds, containing no other elements than oxygen, hydrogen and perhaps nitrogen or sulphur, there is a small group of inorganic resins. For example, silicic acid gels, as well as glass, exhibit some of the properties of organic plastics. (See Chapter 3.) However, the present chapter deals, in the main, with organic compounds of silicon which, although exhibiting many of the characteristics of silicates, are definitely resinous in character. Some of them are soluble in organic solvents. In reviewing the most important inorganic resins, including compounds of silicon, germanium, phosphorus, boron and thallium, it should be borne in mind that they have, despite their rarity, potential commercial significance.<sup>1</sup>

### SILICA

Diatomite and coal when heated together give a product called silica black. Jacobson<sup>2</sup> heated a mixture of silicon dioxide and finely ground coal in a 1-quart iron retort at 600-700°C. for 4 hours. Of the black pulverulent material left in the retort, 43 per cent was fine enough to pass a 200-mesh, and most of the remainder a 100-mesh sieve. The product was not a mechanical mixture but was amorphous and had a composition of 18 per cent carbon, 75.5 per cent silicon dioxide and 6.5 per cent oxides and sulphides. Silica black is insoluble in water and the usual organic solvents. It acts as a clarifier and decolorizer and may be used in ink, stove polish and as a carrier for insecticides.

When silicic acid is dehydrated with heat, a colloidal mass of silicon dioxide known as silica gel is formed. The elasticity and plasticity of acid, neutral and alkaline types of this substance can be measured by bending tests.<sup>3</sup> For samples of the same age, the elastic properties are similar; but the plasticity and shrinkage increase continuously from the acid to the alkaline gels. The freezing-point depression, viscosity, and electrical conductivity of purified sols of silicon dioxide have been determined.<sup>4</sup> From the results it appears that gelatinization begins with polymerization of simple molecules, accompanied by a decrease in the number of free hydrogen ions, the polymerized molecules afterwards coagulating to form a network which imbibes the whole of the liquid. Similarly, other investigators,<sup>5</sup> after a study of viscosities of silicic acid solutions, report that solutions from more highly polymerized esters gel more quickly.

The alkyl silicates are important because of their application in silicon-ester paints. The method of preparing ethyl orthosilicate, which was discovered by

<sup>1</sup> Stacol, an inorganic resin manufactured by Glyco Products, Brooklyn, was put on the market in 1933 (*Plastics*, 1933, 9, 373).

<sup>2</sup> C. A. Jacobson, *Ind. Eng. Chem.*, 1934, 26, 798. U. S. P. 1,940,352, Dec. 19, 1933; *Chem. Abs.*, 1934, 28, 1555.

<sup>3</sup> M. Kröger and K. Fischer, *Kolloid-Z.*, 1929, 47, 10; *Chem. Abs.*, 1929, 23, 1798.

<sup>4</sup> W. D. Treadwell and W. König, *Helv. Chim. Acta*, 1932, 16, 34; *Brit. Chem. Abs. A*, 1933, 348.

<sup>5</sup> R. Signer and H. Gross, *Ann.*, 1932, 499, 158; *Brit. Chem. Abs. A*, 1933, 23. See L. A. Jordan and J. O. Cutter, *J.S.C.I.*, 1935, 54, 89T.

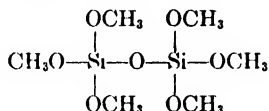
Ebelmen,<sup>6</sup> has been improved by Dearing and Reid.<sup>7</sup> Silicon tetrachloride, free from higher-boiling compounds, is added dropwise to anhydrous alcohol cooled in a freezing mixture and present in 10 per cent excess to insure the reaction of all the chlorine.



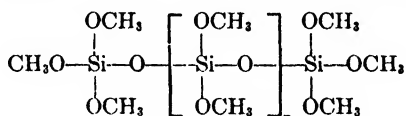
The ester is then fractionated in a vacuum, water being carefully excluded, to give a 70 per cent yield. Other alkyl orthosilicates have been prepared in the same way.<sup>8</sup>

A shallow layer of ethyl orthosilicate reacts readily with water vapor, or water diluted with alcohol, to yield silica gel. A non-aqueous gel is prepared by refluxing a mixture of 4 parts of acetic acid to 1 part of the ester for an hour and allowing it to stand overnight. Excess acetic acid is removed by immersion in dry benzene.

In the alkyl orthosilicate formation from silicon tetrachloride and alcohol, variable quantities of high-boiling, viscous substances are also obtained.<sup>9</sup> Treatment of 1 mol of methyl orthosilicate with 0.5 mol of water leads almost exclusively to the formation of the disilic ester



An increase in the ratio of water to ester results in a compound of the type



in which  $x$  is a function of the ratio. Using 1 mol of water to  $\frac{1}{2}$  mol of alcohol, a product having an approximate molecular weight of 10,000 is obtained.

Inasmuch as alcoholic solutions of silicon esters react with water to form colloiddally dispersed silicon dioxide, silicon-ester paints are feasible. Hydrolyzed silicon esters, which contain about 9 per cent silicon dioxide, penetrate stone yielding a hard protective silica gel.<sup>10</sup> The paint medium is prepared by stirring 351 l. of a solvent ester into 50.7 l. of water in 135 l. of 94 per cent alcohol until solution is obtained and then adding 250 l. of the silicon ester.<sup>11</sup> Titanium dioxide, earth colors or other non-basic pigments are incorporated, and the solution can then be preserved in sealed containers. The essential feature of the paint is its property of hydrolysis, resulting in a coating of silica.<sup>12</sup> The advantages, it has been stated, are that it is compatible with wet plaster, heat resistant, does not blister, is easy to clean, porous (permits breathing of the surface), easy to work and economical. The disadvantages are that it does not adhere to distempers and oil paints and is difficult to store.

The best method of applying a silicon-ester coating is by means of a spray,

<sup>6</sup> Ebelmen, *Ann.*, 1846, 57, 334.

<sup>7</sup> A. W. Dearing and E. E. Reid, *J.A.C.S.*, 1928, 50, 3058.

<sup>8</sup> J. Weiler (*Helv. Phys. Acta*, 1932, 5, 302; *Brit. Chem. Abs. A*, 1933, 1102) has determined the Raman spectra for silicic acid esters.

<sup>9</sup> E. Konrad, O. Bächle and R. Signer, *Ann.*, 1929, 474, 276; *Brit. Chem. Abs. A*, 1930, 461.

<sup>10</sup> G. King, *J. Oil and Colour Chem. Assoc.*, 1930, 13, 28; *Chem. Abs.*, 1930, 24, 2313. See also W. Graulich, *Nitrocellulose*, 1933, 4, 61; *Chem. Abs.*, 1933, 27, 3002.

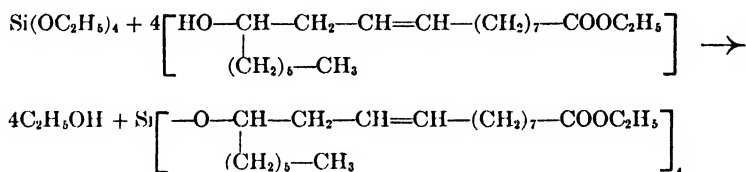
<sup>11</sup> See also G. King and R. Threlfall, *British P.* 290,717, 1927; *Chem. Abs.*, 1929, 23, 942. German P. 553,514, 1927; *Chem. Abs.*, 1928, 26, 5712. French P. 649,782, 1923; *Chem. Abs.*, 1929, 23, 3063.

<sup>12</sup> See also W. Graulich, *Tonind.-Ztg.*, 1933, 57, 677; *Chem. Abs.*, 1934, 28, 1552.

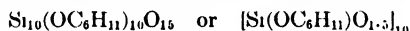
although spreading with a brush is satisfactory.<sup>13</sup> Initial setting, depending on the amount of diluents and atmospheric moisture, takes place in approximately an hour; final setting, which is the completion of the hydrolysis, requires a longer period.

Esters have also been employed in solution as binders in the preparation of porous objects made by mixing powdered silica with calcium carbonate<sup>14</sup> and in the manufacture of insulators from small pieces of mica.<sup>15</sup> In the latter case, methyl orthosilicate in alcoholic solution is hydrolyzed to give an adhesive material which is incorporated with the mica, and the whole is heated under pressure, forming a solid mass.

Oily and viscous silicyl compounds have been prepared<sup>16</sup> by reaction between hydroxycarboxylic acid esters and silicic acid alkyl esters. For example, 10 parts of ethyl ricinoleate are heated with 2 parts of ethyl orthosilicate in a closed container at 150°C. The resulting alcohol and excess ethyl orthosilicate are distilled off *in vacuo*; the product is taken up in ether, washed with water, dried with anhydrous sodium sulphate and the solvent evaporated. The reaction may be written as follows:



Silicon tetrachloride reacts with cyclohexanol to form trichloro-cyclohexanoxy-, dichloro-di(cyclohexanoxy)-and monochloro-tri(cyclohexanoxy)-silicon.<sup>17</sup> The polymeric esters were prepared by shaking the monomolecular esters in absolute ether with dry silver carbonate. The trichloride gave a product of the formula



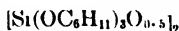
as a white amorphous mass. The dichloride yielded a solid



and an oil



The monochloride formed a compound with the formula



Kipping and his co-workers in their work on silicon have discovered a number of complex compounds, some of which are amorphous or gluc-like. These will be discussed without any attempt to outline their chemistry in detail.

The action<sup>18</sup> of sodium on diphenylsilicon dichloride in toluene solution gives sparingly soluble compounds of the formula  $[\text{Si}(\text{C}_6\text{H}_5)_2]_n$ . In addition a glue-like, readily soluble material is formed. It is believed to be amorphous octaphenyl-cyclosilicotetrasilane,<sup>19</sup> the crystalline form of which is only slightly soluble in cold acetone. The sparingly soluble silicohydrocarbon is converted by diphenylsilicon

<sup>13</sup> W. Graulich, *Nitrocellulose*, 1933, 4, 61; *Chem. Abs.*, 1933, 27, 3092.

<sup>14</sup> G. King, French P. 731,429, to Albright and Wilson, Ltd.; *Chem. Abs.*, 1933, 27, 383.

<sup>15</sup> German P. 593,072, 1934, to Jaroslaw's Erste Glimmerwaren-Fabrik; *Chem. Abs.*, 1934, 28, 3152.

<sup>16</sup> H. Kaufmann, U. S. P. 1,918,338, July 18, 1933; *Chem. Abs.*, 1933, 27, 4879.

<sup>17</sup> R. Signer and H. Gross, *Ann.*, 1931, 488, 56; *Chem. Abs.*, 1931, 25, 5188.

<sup>18</sup> F. S. Kipping and J. E. Sands, *J.C.S.*, 1921, 119, 830.

<sup>19</sup> F. S. Kipping, *J.C.S.*, 1927, 2719.

dichloride into glue-like products.<sup>20</sup> This action takes place only with the reagent itself and does not occur in a diluent, e.g., toluene. The amorphous form of octaphenylcyclotetrasiloxane, dissolved in acetone and treated with alcohol, forms a white plastic precipitate which can be pulled out into long silk-like threads, but these become brittle when the solvent evaporates. The residue from the destructive distillation of the amorphous material, when cold, is a brittle honey-colored resin, insoluble in all the common solvents.<sup>21</sup> If treated with cold chloroform, a small proportion separates in the form of yellow flakes.

Di-*p*-tolylsilicanediol in 5 per cent sodium hydroxide solution precipitates a gluey condensation product.<sup>22</sup> Similarly, when diphenyltolylsilicanediol is treated with hot potassium hydroxide, complex amorphous condensation products are obtained.<sup>23</sup>

Dibenzylsilicon dichloride yields, on heating with sodium in toluene, a small amount of tribenzylsilyl oxide and tetrabenzylsilicane, and a large amount of octabenzylsilicetetran oxide,  $[\text{Si}(\text{CH}_2\text{C}_6\text{H}_5)_2]_4\text{O}$ , a resinous mass.<sup>24</sup> The latter, when precipitated as an oil from its acetone solution with alcohol, hardens to a solid resin. From chloroform, it separates as a blood-red resin, which on treatment with acetic acid forms a colorless, glue-like mass. Octabenzylsilicetetran oxide is also obtained as a highly lustrous, flaky solid by frothing its ethereal solution.

Phenylsilicon trichloride, dissolved in xylene, reacted in a sealed tube at 150°C. with sodium to give a small amount of insoluble and some soluble material. The latter was a pale yellow resin, fractionation of which gave a series of colorless powders and gelatinous substances.<sup>25</sup> They either charred or liquefied over a wide temperature range. Further examination showed that an increase in oxygen content of the compound decreased its solubility in organic solvents. Molecular weight determinations on the xylene-soluble resins gave values between 900 and 9000, corresponding to 6 and up to about 50 silicon atoms in the molecule.

The formation of a similar series of products by the action of sodium in boiling toluene on di-*p*-tolylsilicon dichloride has also been studied.<sup>26</sup> Another illustration of a reaction giving amorphous materials is that occurring between cyclohexyl magnesium bromide and silicon tetrachloride. When the reagents are heated together in ether and distilled at 3-4 mm., cyclohexylsilicon trichloride and dicyclohexylsilicon dichloride are collected. The residue is very viscous and dissolves in ether. On continued heating, frothing occurs and the contents of the flask gradually become solid.<sup>27</sup>

Kipping and Blackburn<sup>28</sup> studied the nitration of tetraphenylsilicane in carbon tetrachloride solution in the absence of sulphuric acid. Ten per cent of the product isolated was a tetranitro derivative which appeared to be tetra-*m*-nitrotetraphenylsilicane, melting at 255°C. The remainder of the crude nitration product was readily soluble in acetone, from which it separated in a glue-like form. From aqueous methyl, ethyl and isopropyl alcohols, however, a colorless powder melting at 90-110°C. was obtained. This, under high magnification, seemed to be composed of globular transparent particles. Their composition approximated that of the tetranitro derivative.

<sup>20</sup> F. S. Kipping, *J.C.S.*, 1923, 123, 2590.

<sup>21</sup> F. S. Kipping and A. G. Murray, *J.C.S.*, 1929, 365.

<sup>22</sup> H. S. Pink and F. S. Kipping, *J.C.S.*, 1923, 123, 2830.

<sup>23</sup> F. S. Kipping and A. G. Murray, *J.C.S.*, 1928, 1427.

<sup>24</sup> A. R. Steele and F. S. Kipping, *J.C.S.*, 1928, 1431.

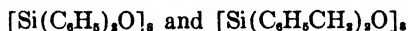
<sup>25</sup> F. S. Kipping, A. G. Murray and J. G. Maltby, *J.C.S.*, 1929, 1180.

<sup>26</sup> A. R. Steele and F. S. Kipping, *J.C.S.*, 1929, 2545.

<sup>27</sup> K. Palmer and F. S. Kipping, *J.C.S.*, 1930, 1020. See also N. W. Cusa and F. S. Kipping, *J.C.S.*, 1932, 2205.

<sup>28</sup> F. S. Kipping and J. C. Blackburn, *J.C.S.*, 1932, 2200.

When diphenyl- and dibenzylchlorosilicane were treated with mercuric oxide, diphenyl- or dibenzylsilicone were not formed but rather thick glue-like substances, soluble in many organic solvents, resulted.<sup>29</sup> These compounds correspond most closely to the following molecular formulas:



Reviewing the compounds of silicon as a group, two reasons for the occurrence of resinous products may be advanced: The first is the tendency of silicon atoms to form chain-like molecules. The second and perhaps the main reason is the presence of organic radicals in the molecule. The further development of the organic chemistry of silicon may lead to the production of cheap and readily prepared derivatives which can be applied as resins or binding agents.<sup>30</sup>

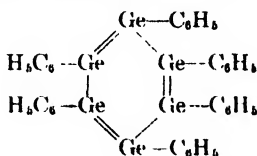
### TITANIUM COMPOUNDS

A number of titanium esters have been prepared, corresponding to the silicon esters already described. Gardner and Bielouss<sup>31</sup> prepared ethyl titanate by the dropwise addition of titanium tetrachloride to a cold solution of sodium ethoxide, with subsequent refluxing. The product was soluble in alcohol, benzene and toluene. Titanium compounds of glycerol and glycol of varying composition were also obtained by the slow addition of titanium tetrachloride to an excess of the corresponding polyhydric alcohol at 80-145°C. The products were soluble in water and alcohol, but not in toluene.

Films of ethyl titanate applied to various surfaces and hydrolyzed *in situ* were unsatisfactory, because they lacked adhesion and continuity. A white-pigmented lacquer was formed on adding titanium glycolate in alcohol (1:4) to a solution of nitrocellulose in butyl acetate. The titanium compound is hydrolyzed under these conditions, forming titanium dioxide.

### GERMANIUM COMPOUNDS

Schwarz and Lewinsohn<sup>32</sup> have made a number of compounds, which suggest the possibility of forming amorphous substances from germanium, among which is the germanium-phenyl ring compound similar to benzene,



This compound was made by the action of metallic sodium on phenylgermanium trichloride in xylene. Monophenyl germanium ( $\text{C}_6\text{H}_5\text{Ge}$ ) was formed, which in turn readily polymerized to form the ring already shown. Germanium tetrachloride reacts with 4 mols of aniline to yield aniline hydrochloride and germanium diphenyldiimide dihydrochloride,  $\text{Ge}(\text{NC}_6\text{H}_5\text{HCl})_2$ , a glassy non-crystalline solid.<sup>33</sup>

<sup>29</sup> L. R. Vyle and F. S. Kipping, *J.C.S.*, 1924, 125, 2616.

<sup>30</sup> N. Heaton (*J. Roy. Soc. Arts*, 1933, 80, 411; *Brit. Chem. Abs.* B, 1932, 392) has pointed out the desirability of silicon-ester paints for artists, inasmuch as inorganic are thought to be more durable than organic materials.

<sup>31</sup> H. A. Gardner and E. Bielouss, *Circ., Am. Paint and Varnish Mfrs. Assoc.*, 1930, 366, 327; *Chem. Abs.*, 1931, 25, 2971.

<sup>32</sup> R. Schwarz and M. Lewinsohn, *Ber.*, 1931, 64, 2352; *Chem. Abs.*, 1932, 26, 704.

<sup>33</sup> J. S. Thomas and W. W. Southwood, *J.C.S.*, 1931, 2033.

## PHOSPHORUS COMPOUNDS

Among the more important resins containing phosphorus are those derived from phosphorus nitrile chloride,  $\text{PNCl}_2$ . Stokes<sup>34</sup> found that when the latter was heated, it polymerized to give rubber-like material. Crude phosphorus nitrile chloride is a buttery mass made up of the primary crystalline bodies,  $(\text{PNCl}_2)_3$  and  $(\text{PNCl}_2)_4$ , together with oily polymers. The latter, when heated at  $200^\circ\text{C}$ ., rapidly yield elastic masses. The crystalline bodies, however, polymerize slowly at  $255^\circ\text{C}$ .; and when the melt is heated for 4 hours at this temperature, it becomes turbid and viscous. On cooling it is amorphous and kneadable like paraffin. The resultant mass melts at  $200^\circ\text{C}$ . After 6 hours heating, polymerization is complete and an inorganic rubber is obtained as an elastic mass. It will no longer melt; and if it is heated to redness, it becomes hard and brittle on cooling. The elastic product, in the pure state, is colorless, transparent, and insoluble in common solvents. In benzene it swells, with the formation of a reversible sol. When it is allowed to stand in the air for a long time, it is transformed into a brittle substance.<sup>35</sup> In his study of the effect of varying degrees of heating on phosphorus nitrile chloride, Renaud<sup>36</sup> reported that some of the polymers have real and others apparent melting points. In the latter case there is a transition from a crystalline form to a clear gel. All of the forms of phosphorus nitrile chloride are brittle at  $-47^\circ\text{C}$ .

Light amber-colored inorganic resins for use in varnishes and insulations have been made by Runyan.<sup>37</sup> One mol of tricresyl phosphate<sup>38</sup> is heated to  $315\text{--}340^\circ\text{C}$  under reflux. At this temperature 3 mols of calcium oxide are added, the heating being temporarily suspended. As the vigor of the resulting reaction subsides, the temperature declines. When it falls to  $245\text{--}260^\circ\text{C}$ ., heating is resumed and continued until the reaction product, on cooling, solidifies to form a resin hard at ordinary temperatures. Trioxymethylene is added during resinification, in amounts corresponding to the phenol released. The addition of linseed oil (5-10 per cent of the weight of the resulting resin) confers toughness. The resin, it has been stated, may be used to impregnate fiber, which is subsequently molded under heat and pressure; or it may be employed in a varnish.

In an attempt to form homophthalyl chloride, homophthalic acid (1 mol) was heated with phosphorus pentachloride (10 per cent in excess of 2 mols) in phosphorus oxychloride as a solvent. The product obtained was 3-chloroisocoumarin. On the other hand, when homophthalic anhydride was substituted for the acid in the reaction, a tarry mass resulted.<sup>39</sup>

Cholesterol, in some of its reactions with phosphorus pentachloride, yields resinous products.<sup>40</sup> When the two substances are mixed in anhydrous benzene, there is an exothermic reaction with a slow steady evolution of hydrochloric acid, the solution meanwhile becoming reddish brown. After 24 hours, the product is washed with water, dried, the benzene evaporated and the residue recrystallized from acetone. There are obtained trichlorocholestane and an unidentified resin. With cholesterol and phosphorus pentachloride in a solid state, cholesteryl chlo-

<sup>34</sup> H. N. Stokes, *Am. Chem. Jour.*, 1895, 17, 275; 1896, 18, 629; 1897, 19, 782.

<sup>35</sup> R. Schenk and G. Römer, *Ber.*, 1924, 57, 1343; *Chem. Abs.*, 1924, 18, 3565.

<sup>36</sup> P. Renaud, *Compt. rend.*, 1932, 194, 2054; *Chem. Abs.*, 1932, 26, 4780.

<sup>37</sup> A. Runyan, U. S. P. 1,938,642, Dec. 12, 1933, to Sinclair Refining Co.; *Chem. Abs.*, 1934, 28, 1559.

<sup>38</sup> Triphenyl phosphate (solid) and tricresyl phosphate (liquid) are high-boiling substances used as plasticizers in making celluloid and in formulating lacquers. Tricresyl phosphate tends to retard combustion, and in this respect resembles some of the highly chlorinated compounds.

<sup>39</sup> W. Davies and H. G. Poole, *J.C.S.*, 1928, 1618.

<sup>40</sup> F. Pirrone, *Gazz. chim. ital.*, 1932, 62, 63; *Chem. Abs.*, 1932, 26, 3260.





and subsequent addition of lead acetate forms a lead salt,  $C_{18}H_{16}O_{12}Pb_2$ , which is a brittle, colorless mass.<sup>48</sup> Glassy masses have also been obtained from the potassium salt derived from allenetetracarboxylic ester.<sup>49</sup>

Thallium ethoxide in benzene, added to a hot solution of tetra-acetylpropane, yields a yellow-colored mass which rapidly turns red.<sup>50</sup> A brown substance precipitates which, on filtration, becomes resinous. Evaporation of the benzene likewise causes resinification of the residue.

<sup>48</sup> E. Benary and R. Schinkopf, *Ber.*, 1923, 56, 354; *J. C. S.*, 1923, 124, 179.

<sup>49</sup> F. Faltis and J. Pirsch, *Ber.*, 1927, 60, 1621; *Chem. Abs.*, 1928, 22, 223.

<sup>50</sup> R. C. Menzies and E. R. Wiltshire, *J.C.S.*, 1931, 2239.

## Chapter 63

### Miscellaneous Resins

This chapter has two purposes. First, it describes some of the applications of synthetic resins in which no particular resin has been specified or where there is presumed to be a latitude of choice. Second, it groups a number of resins which have not come under the scheme of classification adopted in the text. Resinous bodies have resulted in the course of reactions carried out in many researches with organic compounds. Such bodies generally are not the result of an effort to produce them but are none the less interesting to investigators working in the field of synthetic resins. At the time of discovery, it may not be practicable to prepare the substance in quantity by the reaction under investigation and yet under later economic conditions this reaction may be applied to commercial advantage. This chapter, therefore, represents so wide a range that but little attempt has been made at classification, and the reader will find it as heterogeneous as are the resins.

#### TECHNICAL APPLICATIONS

**Various Applications of Resins with Cellulose Derivatives.** Synthetic resins have found a number of applications in conjunction with cellulose derivatives, usually in the production of films.

A liquid- and moisture-proof, transparent and flexible material is formed by coating transparent foils of regenerated cellulose with a cellulose ester lacquer. With the latter is incorporated a solution of a solid or liquid wax or grease, and a natural or synthetic resin in a solvent which is miscible with the cellulose ester lacquer. The applied film is then exposed for a time to a temperature above the softening point of the waxes.<sup>1</sup> An insulating material can be prepared from mineral wool mixed with a binder made of nitrocellulose, cumarone resin, and a solvent.<sup>2</sup> Waterproofing substances, such as natural or synthetic resins, asphalts, paraffins or waxes may also be added to impermeable and insulating compositions made from nitrocellulose varnishes and triaryl phosphates.<sup>3</sup> An insulator resistant to heat, moisture and electricity is likewise obtained by applying a liquid insulating resin to a solid carrier of transparent regenerated cellulose obtained from viscose. The coating can be dried and solidified at any desired temperature.<sup>4</sup>

Surfaces made from insoluble and infusible resins have been suggested as bases for depositing cellulose acetate solutions in film manufacture.<sup>5</sup> Cellulose derivatives may be used similarly for coating spools used in the textile industries, the metal spools being first coated with a natural or synthetic resin.<sup>6</sup> Fibrous material and synthetic resin have also been employed for coating wooden shuttles.<sup>7</sup>

<sup>1</sup> R. Weingand and F. W. Spiecker, British P. 309,017, 1928, to Wolff and Co., Kommandit-Ges. auf Akt.; *Brit. Chem. Abs. B.*, 1930, 11. British P. 318,166, 1929; *Brit. Chem. Abs. B.*, 1930, 318.

<sup>2</sup> French P. 641,487, 1927, to I. G. Farbenind. A.-G.; *Plastics*, 1929, 332.

<sup>3</sup> French P. 645,621, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 1971.

<sup>4</sup> British P. 293,293, 1928, to Elektra-Lack-Werke G.m.b.H.; *Brit. Chem. Abs. B.*, 1929, 404.

<sup>5</sup> British P. 359,390, 1930, to British Celanese, Ltd.; *Chem. Abs.*, 1933, 27, 413.

<sup>6</sup> British P. 311,287, 1929, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B.*, 1930, 899.

<sup>7</sup> A. Christoph, U. S. P. 1,861,593, June 7, 1932; *Chem. Abs.*, 1932, 26, 4190.

Iron, glass or wood surfaces may be covered with a synthetic resin modified by the addition of a cellulose derivative. Further applications of a cellulose ester can be made.<sup>8</sup> Coating compositions are prepared by dissolving cellulose acetate in a low-boiling vehicle consisting of ethyl alcohol, benzene, and ethylene dichloride. Resins, high-boiling solvents, plasticizers, pigments and fillers may then be incorporated.<sup>9</sup> Solutions containing methyl or benzyl cellulose, synthetic resins, plasticizers and stabilizers have been suggested also.<sup>10</sup> The addition of resins to a lacquer containing cellulose acetate, dibutyl tartrate and triphenyl phosphate dissolved in acetone is said to improve its strength and adhesive power.<sup>11</sup>

Synthetic resins of various types may be added in amounts between 1 and 25 per cent to cellulose ethers and esters to increase the tensile strength of artificial filaments, plastic compositions, and adhesives made therefrom.<sup>12</sup> Thus, simulated horse-hair, bristles or straw are prepared by extruding a solution of cellulose ester, resin and plasticizer into an evaporative atmosphere or a coagulating bath.<sup>13</sup> The addition of natural or synthetic resins, which melt above 250°C., to cellulose derivatives reduces the luster of the threads formed by spinning.<sup>14</sup> In the manufacture of artificial silk by the wet-spinning process, soluble synthetic resins are among the materials which may be added to the precipitating bath.<sup>15</sup>

Plinatus<sup>16</sup> employed natural or synthetic resins in conjunction with cellulose esters in the preparation of binders and adhesives. A fusible or soluble synthetic resin may be used also to secure adhesion between a plastic sheet of a cellulose derivative mixed with an organic tartrate, such as dibutyl tartrate, and two sheets of glass.<sup>17</sup> Synthetic resins in a reactive state may be applied to a porous carrier such as paper or fabric, or mixed with film-forming solutions (viscose or cellulose ester solution) to provide films or sheets for adhesive purposes.<sup>18</sup> A binding agent consisting of a solution containing 8-15 per cent of a cellulose derivative and a natural or synthetic resin can be employed in making a moisture-proof, match-igniting composition.<sup>19</sup>

By dissolving higher fatty acid esters of cellulose (such as cellulose distearate) in xylene, with the addition of fatty or mineral oils, waxes and artificial resins Lant and Koreska<sup>20</sup> have prepared varnishes for tennis-racket strings.

The flexibility of synthetic resins capable of being hardened is found to be preserved by incorporating alkyl celluloses.<sup>21</sup> Normally light-sensitive synthetic resins, or coatings containing them, can be darkened by exposure to ultraviolet light. Alternatively, the resin may be darkened during manufacture in the presence of benzoic or salicylic acid as catalyst. Coatings which contain such darkened resins together with cellulose derivatives, especially the acetate, do not change color on further exposure to light.<sup>22</sup>

<sup>8</sup> W. H. Moss, British P. 298,616, 1927, to British Celanese, Ltd.; *Chem. Abs.*, 1929, 23, 3115. Canadian P. 304,295, 1930, to C. Dreyfus; *Chem. Abs.*, 1930, 24, 5516.

<sup>9</sup> British P. 299,792, 1928, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1930, 676.

<sup>10</sup> C. Dreyfus, British P. 309,951, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 789.

<sup>11</sup> W. H. Moss, U. S. P. 1,952,227, Nov. 27, 1934, to Celanese Corp.; *Chem. Abs.*, 1935, 29, 530.

<sup>12</sup> W. H. Moss and B. B. White, British P. 317,457, 1928, to British Celanese, Ltd.; *Chem. Abs.*, 1930, 24, 2291.

<sup>13</sup> C. Dreyfus, British P. 342,340, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 5029.

<sup>14</sup> H. Dreyfus, British P. 346,793, 1929; *Brit. Chem. Abs. B*, 1931, 799.

<sup>15</sup> British P. 310,842, 1928, to Aceta Ges.; *Chem. Abs.*, 1930, 24, 724.

<sup>16</sup> W. Plinatus, British P. 303,855, 1928, to Compagnie française d'exploitation des procédés Plinatus; *Chem. Abs.*, 1929, 23, 4542.

<sup>17</sup> British P. 340,927, 1929, to British Celanese, Ltd.; *Chem. Abs.*, 1931, 25, 4997.

<sup>18</sup> R. Arnot, British P. 333,194, 1929; *Brit. Chem. Abs. B*, 1930, 1062.

<sup>19</sup> S. H. Ledin, British P. 355,901, 1930; *Brit. Chem. Abs. B*, 1931, 1028.

<sup>20</sup> R. Lant and W. Koreska, British P. 343,117, 1929; *Chem. Abs.*, 1931, 25, 4421.

<sup>21</sup> French P. 678,206, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 3663. See also French Patent 681,934, 1929, to Compagnie française pour l'exploitation des procédés Thomson-Houston; *Chem. Abs.*, 1930, 24, 4409.

<sup>22</sup> British P. 303,169, 1928, to British Celanese, Ltd.; *Brit. Chem. Abs. B*, 1930, 779.

**Impregnation of Cellulosic Material with Synthetic Resins.** The treatment of vegetable fiber with synthetic resins offers considerable scope for the fabrication of artificial wood and molded insulating material. For example, a resin-coated board can be obtained by applying a layer of synthetic fusible resin, mixed with fillers, to a fibrous spongy base containing a fusible binder with a low coefficient of expansion (e.g., asphalt). The whole is compacted, and the resin rendered infusible by heat and pressure.<sup>23</sup> In another case, saponified or emulsified hard waxes, such as Montan wax, either alone or mixed with other hard waxes or natural or synthetic resins, can be added to fibrous pulp in quantities up to 35-50 per cent of the weight of dry pulp. The material is then precipitated by the addition of alum, and the pulp-wax mixture is formed into sheets and molded.<sup>24</sup>

Samsonov<sup>25</sup> prepared artificial wood from vegetable materials such as reeds or cane trash with the fibers arranged in one direction, by immersing in a natural or artificial resin and then compressing. Fungicides were incorporated. The steps of solvent-extraction and resin-polymerization in synthetic resin varnish-impregnation processes for wood, tissue paper and cardboard may be conveniently carried out in dry steam. The latter carries away solvents which can subsequently be recovered.<sup>26</sup>

Vulcanized fiber may be impregnated with solutions of substances capable of forming synthetic resins. The development of the latter is thus effected within the material.<sup>27</sup> Regal<sup>28</sup> hydrolyzed paper with sulphuric acid and then treated it with an alkaline solution of a synthetic resin. Precipitation of the resin *in situ* gave an imitation parchment. If glassine paper, made from highly-beaten pulp, is impregnated with a solution of castor oil in benzene, dried, treated with a solution of resin, and dried again, it is rendered transparent, according to Chamberlain and Periam.<sup>29</sup> Flexible sheet material which can be used as a substitute for glass is made by coating gauze or netting with a homogeneous mixture of synthetic resin and cellulose acetate.<sup>30</sup> A paper for cigarette mouthpieces is made by treating thin tissue paper with a synthetic resin.<sup>31</sup>

Impregnation of cellulosic material with synthetic resins may be effected in the following manner: Wood shavings, leaves or woven fabrics, for example, are subjected successively to 1 per cent sodium hydroxide solution at 100°C. and to an aqueous solution of an oxidizing agent, e.g., 5 per cent sulphuric acid and nitric acid. The product is washed and dried after each operation, being finally neutralized with ammonia. It is then impregnated with a synthetic resin solution (or ingredients which will form resins), heated, and pressed to render the resin insoluble.<sup>32</sup> Another instance is the treatment of the fibrous material which is fed to the final presses in the manufacture of pressboard. The wet mass is soaked in alcohol, removed and immediately immersed in a synthetic resin. After drying it is then molded under heat and pressure.<sup>33</sup>

A process developed by Geyer<sup>34</sup> for the production of molded ornamental panels

<sup>23</sup> British P. 291,633, 1927, to Agasote Millboard Co.; *Brit. Chem. Abs. B*, 1928, 638. See also British P. 319,901, 1928; *Chem. Abs.*, 1930, 24, 2624.

<sup>24</sup> H. Friedlander, British P. 262,828, 1926; *Brit. Chem. Abs. B*, 1928, 638.

<sup>25</sup> A. de Samsonov, British P. 353,186, 1930; *Brit. Chem. Abs. B*, 1931, 885. French P. 679,708, 1929; *Chem. Abs.*, 1930, 24, 3877.

<sup>26</sup> D. A. Texier, British P. 329,066, 1929, to Manuf. de machines aux. pour l'electr. et l'ind.; *Brit. Chem. Abs. B*, 1930, 726.

<sup>27</sup> British P. 316,700, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1930, 24, 1906.

<sup>28</sup> A. Regal, U. S. P. 1,843,783, Feb. 2, 1932; *Chem. Abs.*, 1932, 26, 1787.

<sup>29</sup> J. Chamberlain and H. Periam, British P. 323,302, 1928; *Chem. Abs.*, 1930, 24, 3114.

<sup>30</sup> British P. 307,462, 1929, to Brit. Celanese, Ltd.; *Brit. Chem. Abs. B*, 1930, 205.

<sup>31</sup> British P. 294,492, 1927, to Wickel & Co., Kommandit-Ges.; *Chem. Abs.*, 1929, 23, 2035.

<sup>32</sup> British P. 331,851, 1929, to Magnasco, Roggero & Co.; *Chem. Abs.*, 1931, 25, 224.

<sup>33</sup> H. W. H. Warren, C. G. Garton and A. E. Smith, British P. 329,378, 1929, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1930, 780.

<sup>34</sup> H. D. Geyer, U. S. P. 1,780,803, Mar. 11, 1930, to Inlaid Mfg. Co.; *Chem. Abs.*, 1930, 24, 2256.

employs a thin coating of transparent synthetic resin to cover a sheet of paper, on which are colored ornamentations. This is applied to a main body portion of bituminous material. Furniture, boxes and similar articles made of wood, metal, paper-like or ceramic materials may be coated or lined with synthetic resin plates, carrying on the back an intermediate veneer which may be attached by cold casein glue or liquid resin.<sup>35</sup> Panels or backings for oil paintings can be made by impregnating a fibrous base, such as pulp board or superimposed sheets of paper or fabric, with a reactive synthetic resin, and subjecting the product to heat and pressure.<sup>36</sup> Keller<sup>37</sup> suggested synthetic resin compositions for backing advertising sheets and posters. In the painting of wood, use may be made of certain tar oils mixed with a cellulose ester solution and a solution of a natural or synthetic resin, with or without a pigment. The tar oil constitutes 30-50 per cent of the total mixture.<sup>38</sup>

One method of producing carbon paper is by spreading a solution of a synthetic resin on paper, evaporating the solvent and adding a color layer. Softening agents (oils or fats, ethyl phthalate or tricresyl phosphate) may be added to the resin layer.<sup>39</sup> Analogous compositions for transfer purposes comprise coloring substances together with synthetic resins or soluble cellulose products.<sup>40</sup> Horii<sup>41</sup> employed a similar process for the manufacture of stencil sheets. A base of fibrous material, such as yoshino paper, carries an impregnating composition containing a synthetic resin and a softening agent, e.g., stearin and castor oil.

**Applications of Synthetic Resins with Rubber.** Blankets for impression cylinders used in printing may be made of one or several layers of fabric impregnated with rubber, a thick coating of rubber and an outer ink-resisting coating of synthetic resin.<sup>42</sup> Quittner<sup>43</sup> developed a method for producing elastic, waterproof, adherent coatings by treating fibrous material with rubber latex and solutions or emulsions of synthetic resins. The latex and resin dispersions may be applied either jointly or successively.

Sheets made from synthetic rubber, synthetic resin and fillers may be used as substitutes for linoleum, celluloid or horn. Factice, natural rubber, cellulose esters and ethers and dyes may be included in the compositions.<sup>44</sup> A flexible material for making pipes, has the following composition: rubber, 40 parts, sulphur, 3 parts, synthetic resin, 25 parts, graphite, 20 parts, and fillers, 12 parts.<sup>45</sup> Lefebure<sup>46</sup> prepared a hose, resistant to gasoline and other organic solvents, by impregnating outer and inner plies of canvas with a resin, using an intermediate layer of rubber. He also made a rubber flooring by vulcanizing rubber sheets or tiles directly on an intermediate layer of wood, cement or stone which can be secured to a floor base. Synthetic resin binder is placed between the contacting surfaces of the materials.<sup>47</sup> Synthetic or natural rubber mixed with a resin and

<sup>35</sup> F. Oehring, British P. 331,870, 1929; *Chem. Abs.*, 1931, 25, 223

<sup>36</sup> British P. 357,204, 1930, to Hakelite Corp.; *Brit. Chem. Abs. B*, 1931, 1090

<sup>37</sup> A. V. Keller, British P. 325,476, 1928; *Chem. Abs.*, 1930, 24, 4176.

<sup>38</sup> F. K. Jähn, German P. 536,429, 1928, to BvK-Guldenwerke Chem. Fab. A.-G.; *Chem. Abs.*, 1932, 26, 1092.

<sup>39</sup> German P. 520,036, 1928 (addn. to 518,272), 518,273, 518,274 and 516,975, to Firma Günther Wagner; *Chem. Abs.*, 1931, 25, 3837, 3484. See also British P. 307,435, 1927; *Chem. Abs.*, 1930, 24, 3903. British P. 324,859, 1928; *Chem. Abs.*, 1929, 23, 5285.

<sup>40</sup> R. D. Bain and E. G. Nixon, British P. 295,118, 1927, to Lanison Paragon Supply Co., Ltd.; *Chem. Abs.*, 1929, 23, 2001.

<sup>41</sup> S. Horii, U. S. P. 1,698,705, Jan. 8, 1929; *Chem. Abs.*, 1929, 23, 1229. See also H. Simon, British P. 286,466, 1927; *Chem. Abs.*, 1929, 23, 249.

<sup>42</sup> S. A. Brazier and F. W. Warren, British P. 353,947, 1930, to Dunlop Rubber Co., Ltd.; *Chem. Abs.*, 1932, 26, 4145.

<sup>43</sup> H. Quittner, Austrian P. 104,398, 1925; *Brit. Chem. Abs. B*, 1927, 420

<sup>44</sup> British P. 304,612, 1928, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 4848.

<sup>45</sup> J. H. Jalbert, French P. 683,008, 1929; *Chem. Abs.*, 1930, 24, 4597.

<sup>46</sup> V. Lefebure, U. S. P. 1,763,973, June 17, 1930; *Chem. Abs.*, 1930, 24, 3869.

<sup>47</sup> V. Lefebure, British P. 237,981, 1924; *Chem. Abs.*, 1926, 20, 1923.

fillers may be employed as an elastic filling composition for cracks or joints in concrete or wood paving and flooring.<sup>45</sup>

The application of synthetic resin globules with a diameter of less than 1 mm. imparts a frosted appearance or sheen to textile fabrics or rubberized goods.<sup>46</sup> A film of protein (treated to render it resistant to water) is utilized for the attachment of rubber to synthetic resins in the lining of vats, or for cementing tires to wheels.<sup>47</sup> Pratt<sup>48</sup> succeeded in developing a material having rubbery qualities by dispersing a terpene (dipentene, isoprene or their polymers) in water in the presence of a protective colloid. The terpene particles should be about the size of latex particles. The coating of protective colloid is then tanned to prevent rupture of the globules during milling. The product when coagulated forms a rubber-like mass capable of vulcanization. Natural or synthetic resin may be added to give an acetone-soluble constituent.

A coating of synthetic or natural resins may be precipitated on a metallic mold as follows: Dispersions of the substance to be deposited are stabilized by an inorganic acid, base or salt. The latter should be capable of reacting with some constituent in the mold in order to cause deposition of a layer of the agglomerated substance on the surface of the mold. Thus, a mold made of zinc or aluminum may be dipped into such a dispersion, and reaction of the alkali with the metal causes a deposit on the surface of the mold.<sup>49</sup>

**Various Coating Compositions and Impregnated Products.** A method of decorating sheet metal is carried out in the following manner.<sup>50</sup> The sheet is first treated with a coat of resins ground in oil and pigmented with colors. A printed or lithographed design secured to a gum coating on a paper backing is dipped in a liquid composed of ethyl lactate, ethylene chlorhydrin, ethyl alcohol and water. The design is then laid face down on the ground coat, pressed on it, the backing is removed and the decorated sheet is baked. It may then be formed into the desired shape. A suspension in tar oil of synthetic resins capable of being hardened also may be used for coating metals.<sup>51</sup>

The surface hardness of light construction materials, e.g., porous cement, can be increased by a coating of synthetic resin.<sup>52</sup>

Mixtures consisting of synthetic resins and liquid softening agents, such as triaryl phosphates, can be utilized in the preparation of electrical insulating compositions.<sup>53</sup> The coating of layers of paper or woven fabrics with synthetic resins offers a further way of building up such materials.<sup>54</sup> For example, electrical insulating sheets and tubing can be made from fabrics composed of "threads" of spun paper by impregnating with a varnish containing resins.<sup>55</sup> Tubes employed in spinning, or other articles made from fibrous material, may also be impregnated with synthetic resins.<sup>56</sup>

Envelopes for gas cells can be constructed from a material composed of one or more layers of an organic cellulose derivative soluble in organic solvents, and

<sup>45</sup> H. P. Stevens, British P. 349,440, 1930; *Chem. Abs.*, 1932, 26, 2844.

<sup>46</sup> F. Thompson, British P. 348,169, 1930; *Brit. Chem. Abs. B*, 1931, 731.

<sup>47</sup> W. B. Wescott, British P. 309,168, 1928, to Rubber Latex Research Corp.; *Chem. Abs.*, 1930, 24, 528.

<sup>48</sup> W. B. Pratt, U. S. P. 1,671,314, May 29, 1928, to Dispersions Process, Inc.; *Brit. Chem. Abs. B*, 1928, 616.

<sup>49</sup> P. Klein and F. Gabor, British P. 399,737, 1927, to Dunlop Rubber Co.; *Chem. Abs.*, 1929, 23, 3599.

<sup>50</sup> A. O. Johnson, U. S. P. 1,866,110, July 5, 1932, to Meyercoord Co.; *Chem. Abs.*, 1932, 26, 4298.

<sup>51</sup> French P. 714,184, 1931, to Vereinigte Stahlwerke A.-G.; *Chem. Abs.*, 1932, 26, 1563.

<sup>52</sup> French P. 709,157, 1931, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 1412.

<sup>53</sup> C. Thode and A. Benischek, German P. 550,129, 1925, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1932, 26, 4115.

<sup>54</sup> British P. 303,125, 1927, to Micasil A.-G.; *Chem. Abs.*, 1929, 23, 4615.

<sup>55</sup> British P. 341,535 and 342,390, 1929, to Internat. Gen. Electric Co.; *Brit. Chem. Abs. B*, 1931, 305.

<sup>56</sup> British P. 215,726, 1923, to Manuf. de machines aux. pour l'electr. et l'ind.; *Chem. Abs.*, 1924, 18, 3477.

one or more layers of a protein, e.g., casein, glue or gelatine. Softening agents, natural and synthetic resins and fillers may be incorporated.<sup>60</sup> Cellulose fibers, rendered moisture-proof by a varnish of synthetic resin containing a plasticizer, are employed in making dust-bags for vacuum cleaners.<sup>61</sup>

Varnish and lacquer coatings which are said to be resistant to shocks and blows can be produced by incorporating with synthetic resin solutions a hard material such as silicon carbide of grain size between 40 and 100 microns.<sup>62</sup> By dispersing a finely divided insoluble and infusible resin in a ketone or ketonic alcohol solution of a hardenable synthetic resin an enamel can be prepared which may be applied in the cold.<sup>63</sup> An interesting development in this connection is the production of waterproof sandpaper, since the ordinary product usually disintegrates when it becomes wet. A cement is used consisting of rosin (250 parts), glue (60 parts), 87 per cent phenol (75 parts), 56 per cent acetic acid (100 parts), water (100 parts) and benzene (5 parts). This, applied to a backing material, will hold abrasives and is flexible and waterproof. The composition is given a final treatment with formaldehyde solution, dried and coated with linseed oil.<sup>64</sup>

A mixture of fish scales with synthetic resins is recommended as a coating for preserving paint on ships or other articles coming into contact with sea water.<sup>65</sup> Guillemin<sup>66</sup> suggested compositions made by heating together natural or synthetic gums or resins, vegetable oil and added materials (e.g., turpentine, "white spirit" and lead oxide) as waterproofing agents for leather.

Mixtures which contain cellulose esters, graphite or mica, finely ground wood or cork, with additions of resin and pigment have been described as knifing compositions.<sup>67</sup>

Objects of acid-proof material can be constructed of wide-mesh fabric impregnated with liquid synthetic resins, and subsequently hardened by heat.<sup>68</sup> A fire extinguisher consists of a liquid which is a poor conductor of electricity (e.g., carbon tetrachloride, tetrachloroethane) together with aluminum sulphate, varnishes, lacquers and the like which will form a resisting insulating layer on the surface over which it is sprinkled.<sup>69</sup>

**Various Molded Materials.** The baskets or pots of centrifugal apparatus may be made by molding and vulcanizing a mixture of natural or synthetic rubber, sulphur and synthetic resins, with or without filling materials.<sup>70</sup> Another type of basket is constructed of annularly disposed cords, provided with a steel wire core, and bound together with synthetic resin.<sup>71</sup> Resins have also been used for making cages or retaining rings for ball and roller bearings.<sup>72</sup>

Panel plates of pressed synthetic resins, joined by grooved strips, pegs and screws of the same material may be used to build up vessels for holding acids and other liquids.<sup>73</sup> Boorne<sup>74</sup> made articles such as tiles and slabs by molding with heat and pressure a mixture of resin, clay, a basic material (lime), a filler (sand), and water. The process was adapted to give products with colored facings or with decorative "crazed" effects.

<sup>60</sup> British P. 371,604, 1931, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1932, 675.

<sup>61</sup> C. W. Studer, U. S. P. 1,829,618, Oct. 27, 1931, to Hoover Co.; *Brit. Chem. Abs. B*, 1932, 662.

<sup>62</sup> British P. 362,728, 1931, to "Herold" A.-G.; *Brit. Chem. Abs. B*, 1932, 197.

<sup>63</sup> H. Plauson, German P. 578,067, 1933; *Chem. Abs.*, 1933, 27, 4429.

<sup>64</sup> F. J. Crupi, U. S. P. 1,484,750, Feb. 26, 1924, to Herman Behr & Co.; *Chem. Abs.*, 1924, 18, 1370.

<sup>65</sup> French P. 701,213, 1930, to Soc. union France; *Chem. Abs.*, 1931, 25, 3855.

<sup>66</sup> J. J. Guillemin, British P. 272,197, 1926; *Chem. Abs.*, 1928, 22, 1701.

<sup>67</sup> British P. 302,615 and 302,616, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 242.

<sup>68</sup> British P. 276,697, 1927, to I. G. Farbenind. A.-G.; *Brit. Chem. Abs. B*, 1929, 320.

<sup>69</sup> French P. 643,137, 1927, to Société Bon "Non frères; *Chem. Abs.*, 1929, 23, 1484.

<sup>70</sup> British P. 350,855, 1929, to Compagnie Generale d'électricité; *Chem. Abs.*, 1932, 26, 2624.

<sup>71</sup> British P. 355,963, 1931, to Internat. Gen. Elec. Co.; *Brit. Chem. Abs. B*, 1932, 417.

<sup>72</sup> British P. 323,719, 1926, to Compagnie d'applications mécaniques; *Chem. Abs.*, 1928, 22, 4000.

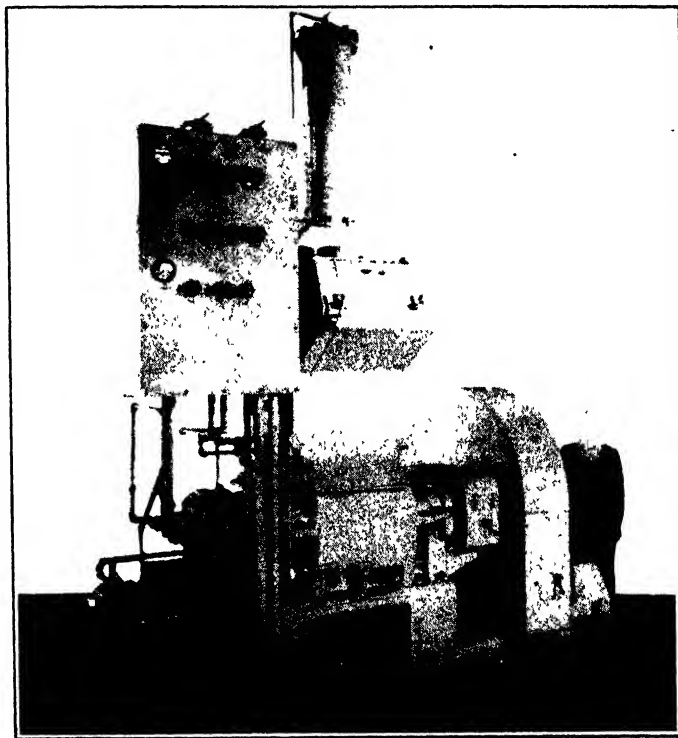
<sup>73</sup> British P. 357,327, 1930, to H. Römmler A.-G.; *Brit. Chem. Abs. B*, 1931, 1079.

<sup>74</sup> W. H. Boorne, British P. 329,382, 1929; *Chem. Abs.*, 1930, 24, 5444.



A magnetic insulating material can be produced by impregnating textile sheets with a mixture of synthetic or natural resin and fillings or fine powder of magnetic material. The sheets are piled and then consolidated under heat and pressure.<sup>75</sup> Powdered magnetic material can also be molded under pressure with magnesium hydroxide and a small quantity of natural or synthetic resin. Magnetic cores for loading coils and transformers are obtained in this way.<sup>76</sup>

Agglomerated horn products may be prepared by hydrating small pieces of horn with hot or cold water, drying superficially *in vacuo* at 15°C. or in an air current at 40-45°C., mixing with a synthetic resin, and then heating at 130-150°C.



Courtesy Furrel-Birmingham Co., Inc.

FIG. 167.—Size 3A Banbury Internal Mixer, Especially Designed for Mixing Plastics.

in a mold under high pressure.<sup>77</sup> Oexmann<sup>78</sup> made disk records from finely powdered horn to which was added a binder such as a natural or artificial resin or casein, and a filler. In order to secure acoustic disks of synthetic resin or cellulose compositions entirely free from solvent, old or newly formed disks are ground up and freed from volatile matter in a vacuum. After this, synthetic resin (or other plasticizing agent) is added and the disks re-formed.<sup>79</sup>

Molded clay, before drying and firing, may be coated with a suspension of colophony (2.5 parts), turpentine (2.5-5 parts) and water (100 parts) with syn-

<sup>75</sup> British P. 308,224, 1929, to British Thomson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1930, 723.

<sup>76</sup> T. Beckinsale and H. J. Allcock, British P. 359,933, 1930, to Callender's Cable & Construction Co., Ltd.; *Chem. Abs.*, 1932, 26, 4144.

<sup>77</sup> G. Bonnard, British P. 362,183, 1930; *Brit. Chem. Abs. B*, 1932, 238.

<sup>78</sup> H. Oexmann, British P. 297,358, 1927; *Chem. Abs.*, 1929, 23, 2794.

<sup>79</sup> French P. 633,790, 1927, to Polyphonwerke A.-G.; *Chem. Abs.*, 1928, 22, 3748.

thetic resin as a binder to secure articles of uniform color.<sup>80</sup> The last stage of firing should be carried out under reducing conditions. So-called "artificial masses" are obtained by treating mud or slime from fresh or salt water (either in its natural moist state or dried in the absence of air) with organic colloidal materials such as natural or synthetic resins.<sup>81</sup> The product is then subjected to the action of hardening or vulcanizing agents. Synthetic resins can also be used as binding agents in the manufacture of refractory articles.<sup>82</sup> Thus, for example, in forming crucibles or muffles, magnesium oxide and crystalline graphite are mixed with a resin (as a binder) and glazing material, and then molded and baked. Molded electrical resistance units can be made from a mixture of graphite, asbestos, clay and a synthetic resin.<sup>83</sup> A material, suggested for the manufacture of buttons, is derived from peat (containing 1 per cent or more of tarry substances) mixed with synthetic resins and powdered blood.<sup>84</sup> Synthetic resins have been applied also in the production of artificial pearls.<sup>85</sup> Moncany<sup>86</sup> developed a moldable plastic material by mixing plaster, fibers and asbestos powder, and incorporating albumin or dextrin. The mixture is molded and baked, then dipped into a bath of water and glycerol, baked again, dipped into a solution of a synthetic resin in alcohol, and baked a third time. The same worker obtained a plastic material from asbestos fiber and paper beaten up with a synthetic resin varnish. Metallic fibers may also be incorporated in the mass.

Synthetic resins may be used as suspension- or dispersion-agents in the removal of coloring matter from waste-paper pulp by agitation with organic solvents.<sup>87</sup>

Rosin employed in the preparation of toilet and medicated soaps can be replaced by an aromatic resinous composition<sup>88</sup> which is made by emulsifying terpenes, synthetic or natural resins and residues from the solvent extraction of flowers ("floral wax"), with glycerol, a solvent such as methyl alcohol or diacetone, and an emulsifier (e.g., ammonium sulphoricinoleate).

Kurz and Albert<sup>89</sup> produced inks for intaglio printing in which pigments are ground in a vehicle prepared as follows: A synthetic resin is dissolved in 96 per cent ethyl alcohol and partly saponified with alkali. Solvents of high-boiling point are added (e.g., methyl cyclohexanone), and the liquid composition is diluted with water.

Alcoholic solutions of natural or synthetic resins can be colored fast to light by basic dyes, such as the triarylmethane dyes, mixed with a small proportion of a strong inorganic or organic acid, an acid salt, or of a nitrate soluble in the varnish.<sup>90</sup> Celluloid, cellulose esters or ethers, or natural and synthetic resins (or their solutions) are also colored by the incorporation of soluble chromium or copper compounds of dyes, particularly of o-hydroxyazo dyes. The materials can

<sup>80</sup> M. Perkiewicz, German P. 545,237, 1930; *Chem. Abs.*, 1932, 26, 3085. French P. 706,561, 1930; *Chem. Abs.*, 1932, 26, 2030.

<sup>81</sup> J. B. Carpsow, R. Lensmann and M. March, French P. 715,238, 1931, to "Kolloidchemie" Studiengesellschaft m.b.H.; *Chem. Abs.*, 1932, 26, 1731. See also British P. 372,917, 1931; *Brit. Chem. Abs. B.*, 1932, 737.

<sup>82</sup> G. S. Diamond, U. S. P. 1,874,961, June 26, 1928, to Electric Refractories Corp.; *Chem. Abs.*, 1928, 22, 3028.

<sup>83</sup> L. E. Powers, U. S. P. 1,816,194, July 28, 1931, to L. Bradley and H. L. Bradley; *Chem. Abs.*, 1931, 25, 5357.

<sup>84</sup> R. Armenault and J. Malet, British P. 344,086, 1928, to Fabriques de produits de chimie organique de Laire; *Chem. Abs.*, 1932, 26, 3344.

<sup>85</sup> Austrian P. 95,897, 1925, to Schicketans & Co.; *Kunststoffe*, 1925, 15, 45.

<sup>86</sup> G. Moncany, French P. 697,435 and 697,436, 1930, to Soc. anon. de decoration architecturale et mobilière; *Chem. Abs.*, 1931, 25, 3137.

<sup>87</sup> H. Scheele, German P. 502,730, 1929; *Chem. Abs.*, 1930, 24, 5497.

<sup>88</sup> P. Villian, British P. 319,804 and 319,832, 1928; *Brit. Chem. Abs. B.*, 1929, 988.

<sup>89</sup> H. Kurz and K. Albert, British P. 371,527, 1931; *Brit. Chem. Abs. B.*, 1932, 637. Austrian P. 124,742, 1931; *Chem. Abs.*, 1932, 26, 860. French P. 711,613, 1931; *Chem. Abs.*, 1932, 26, 1810. German P. 547,443, 1930; *Chem. Abs.*, 1932, 26, 3686.

<sup>90</sup> British P. 295,941, 1927, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 2309.

either be kneaded together on rolls, or solutions in organic solvents of the dye and the resin can be blended.<sup>91</sup>

Highly polymerized fatty pitches, such as stearin pitch, which are almost insoluble in organic solvents, can be rendered readily soluble by mixing with soluble resins or resin esters, and subjecting the mixture to hot rolling.<sup>92</sup> Colloidal suspensions of insoluble resins are rendered stable at all concentrations by the addition of a slightly alkaline aqueous solution of an auxiliary colloid such as casein.<sup>93</sup>

Warren<sup>94</sup> has obtained metallic surfaces on resins by coating with, for instance, silver nitrate and powdered silver, subjecting the mixture to the reducing action of formaldehyde and drying. A hard synthetic resin incorporated with bronze powder may be applied as a coating for metal surfaces.<sup>95</sup> Another procedure consists in mixing the resin with water glass, clay or metallic oxides.<sup>96</sup> After applying to the surface, hardening may be effected by heating in the absence of air.

A polishing composition was prepared by Collard<sup>97</sup> as follows: A mixture of fats or oils (3-10 parts), resins (2-8 parts) and synthetic or natural waxes (2-8 parts) is heated to 110-160°C., and a suspension of a fine grit (e.g., kieselguhr) (25-40 parts) in "white spirit" or turpentine (40-60 parts) is added. Other polishing mixtures have been made incorporating powdered ebonite and an incompletely polymerized resin with abrasives.<sup>98</sup>

Beebe and Herlinger<sup>99</sup> produced a light-sensitive photographic coating composition by introducing iodine (dissolved in benzene) into a varnish. The latter contained resins, metal salts capable of combining with the halogen (e.g., lead resinate) and a solvent such as gasoline. Sufficient halogen is introduced to combine with all the salts present, forming metal halides.

A lithographic plate is made by preparing a sheet of metal with a sensitive area to which is applied a lacquer containing a synthetic resin which is substantially insoluble in solvents such as acetone and benzene.<sup>100</sup> Light-sensitive resin layers for preparing etched metal plates for photomechanical printing can be made from solutions consisting of a resin, a chromate, an organic solvent and a base.<sup>101</sup>

According to Tomkins and Woodman,<sup>102</sup> synthetic resins can be used for preserving fruits and vegetables by sealing the cut surfaces of the stalks.

Gas bubbles do not adhere to floats for indicating density when the latter are made of artificial wax and resin. Such floats are made up of equal parts of synthetic resin and synthetic wax with coloring matter and a varying amount of barium sulphate according to the specific gravity desired.<sup>103</sup>

An interesting method for introducing or eliminating substances from a syn-

<sup>91</sup> W. Müller, K. Holzach and H. Krzikalla, German P. 517,491, 1926, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1931, 25, 2304.

<sup>92</sup> S. E. Israel, German P. 548,348, 1929; *Chem. Abs.*, 1932, 26, 3661.

<sup>93</sup> L. Brauthite, French P. 722,358, 1930; *Chem. Abs.*, 1932, 26, 4191.

<sup>94</sup> A. I. Warren, U. S. P. 1,834,812, Dec. 1, 1932, to British Metallising Co.; *Chem. Abs.*, 1932, 26, 1079.

<sup>95</sup> German P. 529,793, 1925, to Chem. Fabr. Kurt Albert G.m.b.H.; *Chem. Abs.*, 1931, 25, 5135.

<sup>96</sup> K. Loos, M. Lehnig, C. Henning and R. Daxsdorf, British P. 274,333, 1926 and 274,355, 1927; *Chem. Abs.*, 1928, 22, 2072.

<sup>97</sup> J. A. J. Collard, British P. 363,036, 1930; *Brit. Chem. Abs. B*, 1932, 272.

<sup>98</sup> E. L. C. Lotard, French P. 89,267, 1930, addn. to 701,411, 1930; *Chem. Abs.*, 1932, 26, 2288; 1931, 25, 4096.

<sup>99</sup> M. C. Beebe and H. V. Herlinger, U. S. P. 1,804,674, Oct. 26, 1926; *Chem. Abs.*, 1927, 21, 26. See also British P. 270,387, 1928, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1928, 22, 1552.

<sup>100</sup> M. C. Beebe and H. V. Herlinger, U. S. P. 1,820,593, Aug. 25, 1931, to Wadsworth Watch Case Co.; *Chem. Abs.*, 1931, 25, 5741. See also M. C. Beebe, H. V. Herlinger and R. R. Swain, U. S. P. 1,740,061, Dec. 17, 1929; *Chem. Abs.*, 1930, 24, 932.

<sup>101</sup> H. Röhrler, German P. 606,195, 1934; *Chem. Abs.*, 1935, 29, 1341.

<sup>102</sup> R. G. Tomkins and R. M. Woodman, British P. 348,755, 1930; *Chem. Abs.*, 1932, 26, 5158.

<sup>103</sup> British P. 345,846, 1930, to Britannia Batteries, Ltd.; *Brit. Chem. Abs. B*, 1931, 571.

thetic resin (e.g., the removal of catalysts from plastic materials) depends upon the use of an electric current.<sup>104</sup>

Dauler<sup>106</sup> has described a method for transferring resin from a still to portable containers in such a way that the resin after it has solidified in the container may be broken up readily. In filling the containers (drums), a cylindrical filler core is held in position. The withdrawal of the core from the solidified resin causes cracking and leaves a cavity, both of which facilitate the breaking and removal of the material.

#### RESINS NOT PREVIOUSLY CLASSIFIED

**The Production of Certain Resins and Tars.** The formation of a resin or tar either as a principal or as a secondary reaction product is such a familiar aspect of preparative organic chemistry as to need little introduction. One of the problems of the future in the synthetic resin industry is to determine which of these resinous materials have special properties rendering them adaptable to large-scale application. It is for this reason that many references to resinification have already been included in cases where at the moment no likely application of the product exists. The following pages contain numerous further references of this type which do not come into the classification used in this book.

Phenolphthalein was first prepared by Baeyer<sup>106</sup> in 1871 and was shown several years later to be di-p-dihydroxydiphenylphthalide. When heated to 250-253°C. this compound melts to a clear liquid, and on cooling to 217°C. solidifies to a glass-like mass.<sup>107</sup> The latter appears to be a polymeric form of phenolphthalein. Several interesting resinous derivatives have been made from the phthalide. Maxorov<sup>108</sup> has described a synthetic resin ("Alkalit") obtained by heating the sodium salt of phenolphthalein with toluoyl chloride. When dissolved in oil this gives an almost colorless, transparent, glossy, water-resistant film which is also very resistant to mineral acids and caustic alkalies. Molecular weight determinations<sup>109</sup> of phenolphthalein-o-toluate and m-toluate show that these resins are monomeric. Fused phenolphthalein itself reverts to the crystalline form when used in films. A variety of di-esters and di-ethers of phenolphthalein are known and, with the exception of the di-m-methylbenzyl ether, all exist in a crystalline form and are converted by fusion or by evaporation of their concentrated solutions into colorless resins which crystallize more or less easily on keeping.<sup>110</sup> The ease of conversion to the crystalline state decreases with increasing weight of the chain, and is greater for esters than ethers. The o- and m-tolylates could not be made to crystallize. Their alkali-resistance was greater than that of many natural and synthetic resins.

Other substances allied to phenolphthalein have been found to be amorphous. Thus, catecholsulphonephthalein, described by Wood<sup>111</sup> is an amorphous deep purple solid which is moderately hygroscopic. Phenolphthalein monomethyl ether<sup>112</sup> crystallizes with solvent of crystallization (e.g., one-half a molecule of toluene). After the solvent has been removed by heating, the molten mass solidifies to a

<sup>104</sup> French P. 644,077, 1927, to Soc. anon. pour l'ind. chim. à Bâle; *Chem. Abs.*, 1929, 23, 1702.

<sup>106</sup> H. N. Dauler, U. S. P. 1,878,267, Sept. 20, 1932; *Chem. Abs.*, 1933, 27, 435.

<sup>108</sup> A. Baeyer, *Ber.*, 1871, 4, 658; *J.C.S.*, 1871, 910; *Ber.*, 1876, 9, 1230; *Chem. Zentr.*, 1876, 7, 740; *Ann.*, 1880, 202, 68; *Chem. Zentr.*, 1880, 11, 348.

<sup>107</sup> Erdmann, *Org. Preparatenkunde*, 1894, 327. W. Herzog and J. Kreidl, *Z. angew. chem.*, 1922, 35, 641.

<sup>109</sup> B. Maxorov, *Bull. Plastmässtroj*, 1931 (1-2); *Farbe u. Lack*, 1932, 223; *Chem. Abs.*, 1932, 26, 5220.

<sup>110</sup> W. Herzog, *Farben-Chem.*, 1933, 4, 8; *Brit. Chem. Abs. B.*, 1933, 199.

<sup>111</sup> N. D. Zelinsky and B. W. Maxorov, *Ind. Eng. Chem.*, 1932, 24, 63.

<sup>112</sup> C. B. Wood, *J.A.C.S.*, 1930, 52, 8463.

<sup>113</sup> H. Lund, *J.C.S.*, 1928, 1872.

glass-like substance which may be kept for months without crystallizing. Ebert<sup>118</sup> prepared a yellow amorphous phenolphthalein melting above 256°C. by extracting partially purified yellow amorphous phenolphthalein with a solvent such as butyl alcohol.

Terpenes and allied products extracted from various parts of plants such as the wood, leaves and seed have a strong tendency to polymerize or oxidize, yielding gummy and resinous products. Condensation of turpentine with formaldehyde has already been mentioned. (See Chapter 37.)

Grognot<sup>114</sup> surveyed many types of resins, for instance, that from oil of sweet almonds. This resin was obtained by adding, with cooling, sufficient phosphorus pentoxide to the oil to make a viscous syrup and allowing the mixture to stand a few days. When it had become a hard brown mass it was washed with hot water and heated on a water bath to remove excess essential oil. The residue was a brittle mass similar to colophony, and had an empirical formula identical with that of the  $\alpha$ -resin of benzoin. From an alcoholic solution the product could be precipitated by either dilute hydrochloric acid or alcoholic lead acetate solution. Oil of rue yielded a deep brown resin when treated as above.

Oil of anise resinified upon treatment with warm iodic acid, iodine and potash. Oxidation appeared to have occurred, and fusion with potash yielded a small amount of what seemed to be anisic acid.<sup>115</sup>

According to Barth,<sup>116</sup> treatment of oil of turpentine, lavender, or juniper with alcoholic potash, followed by neutralization with dilute sulphuric acid yielded resins which were soluble in ether, similar to colophony and had the formula  $C_{30}H_{50}O_3$ . They were unaffected by further treatment with potash, and were fairly stable to oxidation, though the turpentine resin was converted slowly into fatty acids and a camphoresinic acid analogue. Barth also suggested the possible close relationship of tannins to these resins.

Methyl salicylate (oil of wintergreen) heated in a bomb at 340-350°C. for several hours gives a 60-70 per cent yield of anisole, 15 per cent of phenol and some resin.<sup>117</sup>

Considerable resin formation takes place in the electrochemical oxidation of cymene (a constituent of such essential oils as oil of caraway and lemon) in sulphuric acid-acetone solution.<sup>118</sup> Acetone when heated for 4 hours at 150°C. with zinc and vinyl bromide yields a mixture of butadiene, isoprene, terpenes and polyterpenes.<sup>119</sup>

Many miscellaneous reactions of aromatic and aliphatic compounds lead to tar formation. Complex pitch-like products are obtained by heating diphenyl ether with sodium at 180-200°C.<sup>120</sup> The preparation of dibenzal succinic acid (from benzaldehyde and ethyl succinate) is accompanied by the formation of considerable resin.<sup>121</sup> cis-Decahydronaphthalene-2-carboxylic acid has been stated to be a resin.<sup>122</sup> Oxidation of dimeric triphenylallene with chromic acid gives a product containing 20 per cent of resinous bodies.<sup>123</sup> Phenylbutadiene chloride was found by Muskat and Huggins<sup>124</sup> to polymerize readily on refluxing. The etherification

<sup>118</sup> J. Ebert, U. S. P. 1,711,048, Apr. 30, 1929, to W. Payne and R. Anderson; *Chem. Abs.*, 1929, 23, 2990.

<sup>114</sup> L. Grognot, *Rev. gen. chim.*, 1907, 10, 49; *Chem. Abs.*, 1907, 1, 1179.

<sup>115</sup> H. Hlasiwetz, *Ann.*, 1866, 139, 91.

<sup>116</sup> L. Barth, *Bull. soc. chim.*, 1868, 70. See also L. Grognot, *loc. cit.*

<sup>117</sup> U. Ipatiev, N. Orlov and A. Petrov, *Bull. soc. chim.*, 1926, 39, 664; *Chem. Abs.*, 1927, 21, 1805.

<sup>118</sup> F. Fichter and J. Meyer, *Helv. Chim. Acta*, 1925, 8, 74; *Chem. Abs.*, 1925, 19, 1251.

<sup>119</sup> F. Leibbrandt, German P. 346,700, 1919; *J.S.C.I.*, 1922, 41, 270A.

<sup>120</sup> P. Schorrigin, *Ber.*, 1923, 56, 176; *J.C.S.*, 1923, 124 (1), 207.

<sup>121</sup> H. Stobbe, G. Ljungren and J. Freyberg, *Ber.*, 1926, 59, 270.

<sup>122</sup> I. W. Borsche and E. Lange, *Ann.*, 1923, 434, 219; *J.C.S.*, 1924, 126 (1), 32.

<sup>123</sup> F. Straus and M. Ehrenstein, *Ann.*, 1925, 442, 93; *Chem. Abs.*, 1925, 19, 1410.

<sup>124</sup> I. E. Muskat and K. A. Huggins, *J.A.C.S.*, 1929, 51, 2496.

of ethylene glycol to dioxane in presence of ferric sulphate leads to the formation of much tarry matter.<sup>126</sup> Resin formation has been noticed also in the preparation of quinine-amine phthalate and phthalyl quinine-amine picrate and of other compounds of this group.<sup>126</sup>

Knapp<sup>127</sup> reports that gummy substances are present in the reaction products from o-phthaloyl chloride, benzyl acetate and aluminum chloride, dissolved in carbon disulphide. According to Borsche and Thiele,<sup>128</sup> 3-phenyl-2-pentene-1,5-oxide changes on standing to a white resin. Treatment of heptene or isohexene with perbenzoic acid in ether yields the corresponding oxides which resinify in the presence of zinc chloride.<sup>129</sup> Senderens<sup>130</sup> observed that cyclohexane-1,2-diol is converted into a resin by concentrated sulphuric acid at 110°C. Humic acid, from coal, when treated with 72 per cent sulphuric acid yields 1.8 per cent of an orange-red lacquer-like substance.<sup>131</sup> Guest found that ethylmagnesium iodide reacts with dipropargyl methylene ether, forming a resin insoluble both in ether and in benzene.<sup>132</sup> The thermal decomposition of phenyl fumarate yields first phenyl cinnamate and subsequently stilbene; substituents in the phenyl group lead to formation of resinous products.<sup>133</sup>

A material of a Peru-balsam type is formed by dissolving condensation products from benzoic and cresotic acid derivatives in benzyl benzoate or benzyl alcohol. Thus, powdered sodium cresotate may be added slowly to a cold mixture of benzoyl chloride, benzene and alcohol at 35°C. Calcium carbonate is then added; and after 24 hours the mixture is warmed to 60°C. with addition of alcohol and benzene, and filtered. The solvents are slowly distilled off; and on further heating of the residue at 60°C. for several hours, a soft resin is obtained. It is only slightly volatile in the cold and dissolves in benzyl benzoate and benzyl alcohol.<sup>134</sup> Heating gelatine and creosote to 160-250°C. yields a resin.<sup>135</sup>

Burgess<sup>136</sup> utilized alginic acid, obtained from sea weed, together with paraffin wax in the preparation of a waterproofing material. The process is illustrated by the following example: 300 grams of kelp containing 30 grams of solid is dissolved in 10 cc. of ammonia and 300 cc. of water. Fifteen grams of paraffin wax dissolved in 40 cc. of carbon tetrachloride are then added, together with 3 grams of copper powder. The charge is heated under reflux at 80-90°C. for 15 hours and the product filtered, washed and dried. It may then be extracted with carbon tetrachloride, and the resulting solution evaporated. A calcium alginate may be used also for the manufacture of a non-shatterable glass.<sup>137</sup> Alginate which has been extracted from marine algae has been esterified with a mixture of sulphuric and nitric acids or sulphuric and acetic acids. The resulting nitrate and acetate esters have been suggested as substitutes for nitrocellulose and cellulose acetate.<sup>138</sup> Reaction between carvacrol, malic acid and concentrated sulphuric acid results in resinification.<sup>139a</sup>

<sup>126</sup> J. van Alphen, *Rec. trav. chim.*, 1930, 49, 1040; *Chem. Abs.*, 1931, 25, 75. See J. V. Braun, A. Heymons and G. Manz, *Ber.*, 1931, 64, 227; *Chem. Abs.*, 1931, 25, 3345. See also T. W. Evans and W. M. Dehn, *J.A.C.S.*, 1929, 51, 3651.

<sup>127</sup> S. Fränkel, C. Trutt, M. Mehrer and O. Herschmann, *Ber.*, 1925, 58, 544.

<sup>128</sup> W. Knapp, *Monatsh.*, 1931, 58, 176; *Brit. Chem. Abs. A*, 1931, 1292. See also F. F. Blick and O. J. Weinkauff, *J.A.C.S.*, 1933, 54, 1446.

<sup>129</sup> W. Borsche and K. Thiele, *Ber.*, 1923, 56, 2012; *Chem. Abs.*, 1924, 18, 688.

<sup>130</sup> J. Levy and R. Pernot, *Bull. soc. chim.*, 1931, 49, 1838; *Brit. Chem. Abs. A*, 1932, 363.

<sup>131</sup> J. B. Senderens, *Compt. rend.*, 1923, 177, 1188; *Chem. Abs.*, 1924, 18, 823.

<sup>132</sup> H. Tropach and A. Schellenberg, *Ges. Abh. Kennn. Kohle*, 1921, 6, 191; *Chem. Abs.*, 1924, 18, 2872.

<sup>133</sup> H. H. Guest, *J.A.C.S.*, 1923, 45, 1804.

<sup>134</sup> R. Anschütz, *Ber.*, 1927, 60, 1320; *Chem. Abs.*, 1927, 21, 2893.

<sup>135</sup> O. Schmatolla, German P. 419,732, 1924; *Brit. Chem. Abs. B*, 1926, 299.

<sup>136</sup> H. Deitchman, U. S. P. 1,937,813, Dec. 5, 1933; *Chem. Abs.*, 1934, 28, 1156.

<sup>137</sup> L. L. Burgess, U. S. P. 1,729,993, Oct. 1, 1929, to Plastic, Inc.; *Chem. Abs.*, 1929, 23, 5568.

<sup>138</sup> M. J. Walsh, U. S. P. 1,923,245, Aug. 22, 1933, to Kelco Co.; *Chem. Abs.*, 1933, 27, 5163.

<sup>139</sup> T. Gohda, French P. 767,877, 1934; *Chem. Abs.*, 1935, 29, 475.

<sup>139a</sup> S. Shljivic and S. Lebedev, *Bull. soc. chim. roy. Yougoslav*, 1933, 4, 133; *Chem. Abs.*, 1934, 28, 6708.

An oily liquid product formed in the catalytic reaction between carbon monoxide and hydrogen yields, when condensed with hydrochloric acid, an oil resembling turpentine oil. If zinc chloride is used as the condensing agent, a resinous body is formed in addition to the oil.<sup>139</sup> The initial oily liquid is fractionated before carrying out the condensation reactions. The residue from fractionation may be purified and employed as a resin for lacquers and varnishes.<sup>140</sup>

A lacquer base was prepared by Pierson<sup>141</sup> from gummy leather made by dipping leather in dilute sulphuric acid to which was added urea, ethylene glycol and phenol. Prior to using, the base is dissolved in a mixture of acetone and ethyl acetate. Rosicki<sup>142</sup> heated isosuccinic acid (1 part), resorcinol (2 parts) and sulphuric acid (1 part) at 120-150°C. for 4 hours. The resulting mass was purified by dissolving in alkali and precipitating with acid; it was found to be soluble in alcohol, ether and alkalies. With lead, a red lacquer was produced.

Bills<sup>143</sup> noted when a solution of cholesterol ( $C_{27}H_{46}O$ ) in carbon tetrachloride, benzene or xylene was boiled with previously ignited fuller's earth colored resinous products were formed and adsorbed on the fuller's earth. The resin could be extracted with ether or acetone, and was found to have antirachitic properties. Cholesterol develops chromogenic properties similar to "oxycholesterol" when heated, the product being brown and resinous.<sup>144</sup> A yellow resinous substance may also be extracted from cholesterol which has been exposed to ultraviolet rays.<sup>145</sup>

The monomethyl ether of chitin was obtained in small yields by repeated methylations. When hydrochloric acid was used to swell the chitin before treatment with dimethyl sulphate, a slimy, difficultly filtered mass was secured. On drying, a horn-like product, which could be pulverized, resulted.<sup>146</sup> Acetylation of chitin yielded a dark-brown amorphous acetyl derivative which was soluble in formic acid or 50 per cent resorcinol solution, but insoluble in other organic solvents.<sup>147</sup> When dissolved in nitric acid (sp.gr. 1.5) and the solution diluted with water, a crumbly precipitate of nitrochitin acetate is obtained.

<sup>139</sup> British P. 244,830, 1924, to Badische Anilin & Soda Fabrik; *Chem. Abs.*, 1927, 21, 307.

<sup>140</sup> A. Eisenhut and A. Auerhahn, U. S. P. 1,704,732, Mar. 12, 1929, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1929, 23, 2000.

<sup>141</sup> W. C. Pierson, U. S. P. 1,899,054, Feb. 28, 1933, to Leagum Corp of Delaware; *Chem. Abs.*, 1933, 27, 2830. See also P. C. Christensen, U. S. P. 1,901,145, Mar. 14, 1933; *Brit. Chem. Abs. B*, 1933, 1020.

<sup>142</sup> J. Rosicki, *Ber.*, 1880, 23, 208; *Chem. Zentr.*, 1880, 205.

<sup>143</sup> C. E. Bills, *J. Biol. Chem.*, 1926, 67, 753; *Chem. Abs.*, 1926, 20, 2354.

<sup>144</sup> T. Moore and S. Willmott, *Biochem. J.*, 1927, 21, 585; *Chem. Abs.*, 1927, 21, 3064.

<sup>145</sup> M. H. Cahan, *Proc. Inst. Med., Chicago*, 1926, 1; *Brit. Chem. Abs. A*, 1928, 1406.

<sup>146</sup> P. Schorigin and N. N. Makarowa-Semljanskaja, *Ber.*, 1935, 68, 969.

<sup>147</sup> P. Schorigin and E. Hait, *Ber.*, 1935, 68, 971.

## Chapter 64

# Analytical and Physical Tests of Synthetic Resins

A discussion of the chemistry of synthetic resins and their plastics rightly concentrates on synthesis or production, but some mention should be made of analytical and identification methods, which are usually qualitative. Supplemental investigations may include quantitative measurements such as acid or iodine value, together with physical and electrical tests, but these are most commonly used for control during manufacture.<sup>1</sup>

Despite the relative scarcity, valuable information on specific phases of analysis has been published by Gardner,<sup>2</sup> Van Heuckeroth,<sup>3</sup> and others<sup>4</sup> while Abraham<sup>5</sup> has described the examination of plastic products made with a bituminous base. In certain cases the identification methods used by Ward, Jordan and Fulweiler in studying the composition of gums formed in gas distribution systems may be helpful.<sup>6</sup> However, the scheme of analysis proposed by Bradley<sup>7</sup> is perhaps the most pertinent although he dealt principally with resins in solution.

### ANALYTICAL SCHEME

Systematic grouping of the various synthetic resins is desirable to keep the work from becoming unnecessarily involved. The following arrangement<sup>8</sup> may be of value as, in almost every case, certain possibilities can be eliminated at the outset.

**1. Polybasic Acid Poly-Esters.** These compositions are easily saponifiable, yielding the original constituents or their salts. The saponification number ranges between 200 and 600. The resins are usually soluble with difficulty in petroleum hydrocarbons and ethanol, but ketones, esters or ether-alcohols are more effective. Their density is generally found to be between 1.10 and 1.42, while the refractive index varies from 1.54 to 1.59. Strong fusion will probably give sub-

<sup>1</sup> Detailed descriptions of all analytical methods are obviously precluded in this text, but selection of the most pertinent procedures should be facilitated by the summaries given.

<sup>2</sup> H. A. Gardner, "Physical and Chemical Examination of Paints, Varnish and Lacquers," 5th Ed., Inst. Paint & Varnish Research, Washington, D. C., 1930.

<sup>3</sup> A. W. Van Heuckeroth, "Physical Properties of Synthetic Resins in Lacquers," *Amer. Paint, Varnish Mfrs. Assn., Circ.*, 1930, 369, 354; *Brit. Chem. Abs. B*, 1930, 1119. Resins on the American market were examined for acid value, softening point, color, solubility and behavior in lacquers. Trade names, chemical classification, and viscosity results were given in most cases.

<sup>4</sup> A. L. Abonyi, *Kunststoffe*, 1926, 16, 30; *Plastics*, 1926, 2, 206; determination of amount of phenolic resin in solution, especially by density measurements. J. Scheiber, *Farbe u. Lack*, 1929, 86, 102; *Pine Inst. Amer. Abs.*, 1929, 3, 55; principles in the determination of synthetic resins. J. H. Frydlander, *Rev. prod. chim.*, 1932, 35, 125; *Chem. Abs.*, 1932, 26, 6163; methods for detection and identification of synthetic resins. T. Ruemele, *Kunststoffe*, 1933, 23, 100; *Chem. Abs.*, 1933, 27, 3835; simple tests for phenol-formaldehyde and urea-formaldehyde resins and genuine amber. A. B. Lorges, *Rev. chim. ind.*, 1929, 38, 180, 198; *Chem. Abs.*, 1929, 23, 5337; analysis and examination of formo-phenolic resins. W. R. Ormandy and E. C. Craven, *J.S.C.I.*, 1923, 42, 181; analytical methods in phenol-formaldehyde condensate manufacture. J. Scheiber, *Farbe u. Lack*, 1933, 353, 376; *Brit. Chem. Abs. B*, 1933, 799; analysis of oil varnishes. W. Wahl, *Plast. Massen*, 1932, 1, 184, 209, 227; 2, 5, 30, 54; *Brit. Chem. Abs. B*, 1932, 1091; physical properties of the constituents of synthetic resin mixtures.

<sup>5</sup> H. Abraham, "Asphalt and Allied Substances," 2nd Ed., D. Van Nostrand Co., New York, 1920.

<sup>6</sup> A. L. Ward, C. W. Jordan and W. H. Fulweiler, *Ind. Eng. Chem.*, 1932, 24, 969; 1932, 24, 1232; 1933, 25, 1224. This series of articles discusses the methods which were employed to show that styrene and indene were the parent substances of most of the samples of liquid-phase gum studied.

<sup>7</sup> T. F. Bradley, *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 304.

<sup>8</sup> T. F. Bradley, *loc. cit.*



limates of phthalic anhydride. In commercial products these resins are most often encountered in nitrocellulose lacquers, enamels, varnishes, paints and primers, frequently in conjunction with aromatic hydrocarbons.\*

**2. Phenol-Aldehyde Condensation Products.** These resins vary from viscous liquids to hard, brittle solids. When modified by large proportions of rosin or fatty acids, they are soluble in petroleum hydrocarbons, and are readily saponified. However, if rosin or fatty acids are not present, saponification is difficult, and aromatic hydrocarbons, ketones and esters are the usual solvents. If unmodified the density will probably lie between 1.20 and 1.28, while the refractive index ranges from 1.62 to 1.69. When heated, a marked odor of phenols, cresols, or formaldehyde may be liberated, and further indications are given by a color reaction in the case of phenols.<sup>10</sup> While resins of this type may be occasionally found in nitrocellulose lacquers, they are more frequently modified and employed in oil varnishes

**3. Cumarone-Indene Polymers.** Unless modified by rosin or fatty acids, these resins are non-saponifiable and are generally insoluble in ethanol. They are, however, soluble in acetone, hydrocarbons, and many esters, and are more easily dissolved in petroleum hydrocarbons than the two groups previously described. The density will probably be between 1.10 to 1.15 but may fall as low as 1.05. Destructive distillation may liberate cumarone and indene, and color reactions are of value. The usual applications of these resins are as bases for spirit varnishes, paints and enamels, especially when maximum alkali-resistance is desired. They may frequently be used with tung oil.<sup>11</sup>

**4. Vinyl Polymers.** In some cases such resins are partially saponifiable and are usually characterized by a water-white or pale straw color. Physically, they may vary from rubbery masses to hard, tough solids which are ordinarily soluble in acetone, ethyl acetate, benzene and toluene, although insoluble in petroleum hydrocarbons. Upon the application of heat, charring takes place, and a distinctive odor is emitted. The density is usually greater than 1.15, and a low refractive index, 1.47 to 1.48, points strongly to the vinyl acetate types. These polymers may also be detected by color reaction. While the resins are seldom utilized with oils in varnishes, they may be found in lacquers with or without nitrocellulose.<sup>12</sup>

**5. Chlorobiphenyls.** Molten caustic can be employed to decompose these resins by fusion, but saponification is difficult unless they are modified by rosin or oils. The solubility in organic solvents, alcohols, ketones, esters and hydrocarbons, is higher than any other group of synthetic resins with the exception of the cyclohexanone-formaldehyde types. At normal temperature, chlorobiphenyls may be found in the form of thin liquids, hard and brittle masses, or semi-crystalline substances which melt readily. The refractive index varies between 1.612 and 1.71 with a density of 1.14 to 1.80. Chlorine may be indicated qualitatively by sodium fusion. Resins of this class are frequently found in either lacquers or varnishes.<sup>13</sup>

\* Representative compounds which are involved in the formation of polybasic acid poly-esters are phthalic anhydride, glycerol, rosin, ethylene or diethylene glycols, pentaerythritol, monohydric alcohols, benzoic acid, succinic acid, maleic acid, malic acid, citric acid, tartaric acid, adipic acid or its higher homologues, other polyhydric alcohols, and higher fatty acids.

<sup>10</sup> Typical constituents of phenol-aldehyde condensation products are phenol, cresols, xylenols, formaldehyde, rosin, glycerol, higher fatty acids, high-boiling tar acids, polyhydric phenols, furfural, acetaldehyde, and ortho- and para-hydroxybiphenyls.

<sup>11</sup> See Chapter 7.

<sup>12</sup> Compounds which are commonly employed in vinyl resin mixtures are vinyl chloride or vinyl acetate polymers, polystyrene, formaldehyde, and cyclohexanone aldehyde.

<sup>13</sup> Chlorinated biphenyl, rosin or rosin ester, and the higher fatty acids are the usual constituents of chlorobiphenyl varnishes and lacquers.

**6. Sulphonamide-Aldehyde Resins.** The color of this group ranges from water-white to pale straw, while the viscosity may be either that of a thick liquid or a semi-crystalline solid. Typical examples of this type have shown a density of 1.35 and a refractive index of 1.596. Sodium fusion may be employed in qualitative tests for sulphur and nitrogen. While the resins are generally soluble in esters, ketones and aromatic hydrocarbons, they are insoluble in ethanol and petroleum hydrocarbons. The condensation product of toluene sulphonamide and formaldehyde may be taken as illustrative of this class.

**7. Urea-Formaldehyde Resins.** The water-white resins may contain urea, thiourea and formaldehyde in combination. As marketed commercially, the products are hard solids, insoluble in water and all common organic solvents; although some of the intermediate condensates may be used as cements or adhesives in aqueous solution. A density approximating 1.48 and a refractive index of 1.66 may be regarded as usual for the harder grades.

**8. Cyclohexanone-Formaldehyde Resins.** Such resins may be distinguished by high solubility in organic solvents, including ethanol, hydrocarbons and oils. They tend to be somewhat hard and brittle and of a pale lemon color. An odor of cyclohexanones or formaldehyde may be detected during fusion. Specimens have given values of 1.207 for density and 1.544 as the refractive index.

In summary, it may be suggested that the resin is synthetic if the density is over 1.15 although it may contain a natural modifying agent. If between 1.10 and 1.15 it is probably a cumarone-indene polymer, shellac or a modified synthetic of another type, and if less than 1.10 it is likely to be either wholly or largely a natural resin. The refractive index and density together give a better indication than either alone, since most synthetic resins are higher in refractive index than the natural materials, with the exception of some cyclohexanone-formaldehyde resins, which are about equal, and some vinyl polymers, especially the acetates, which are lower.<sup>14</sup>

#### PREPARATION OF SAMPLES FOR EXAMINATION

It is, of course, desirable to isolate the resin as far as practicable before attempting analysis. If a commercial product, any pigment present must necessarily be removed either by centrifuging or filtration. Rosin and certain plasticizers, such as phthalates or phosphates, should be extracted with petroleum ether, and the residue, containing most of the synthetic resins, may be subjected to a general examination for appearance, hardness and solubility. Before the qualitative chemical procedure is undertaken, the density<sup>15</sup> and refractive index<sup>16</sup> should be determined.

#### QUALITATIVE TESTS

Qualitative chemical tests may be conducted on these resin residues for halogens, nitrogen and sulphur, using the standard sodium fusion method as described by Mulliken.<sup>17</sup> Behavior of the sample on heating with sodium, or with 50 per cent aqueous sodium hydroxide, is carefully noted, particular attention being paid

<sup>14</sup> Synthetic resins of high refractive index (1.70-1.90) are of value in petrography. See A. E. Alexander, *Ind. Eng. Chem., News Ed.*, 1935, 13, 330.

<sup>15</sup> T. F. Bradley has suggested direct weighing in air and in water for large pieces of resin, the pycnometer for less solid material, and immersion in salt solutions of known density for very small pieces and for films. W. Maas (*Chem. Fabrik*, 1931, 318; *Chem. Abs.*, 1931, 25, 5062) has used tinfoil crucibles and a Westphal balance for bitumens and resins.

<sup>16</sup> The Abbe refractometer may be used, but microscopic methods using reference liquids as given by E. M. Chamot and C. W. Mason (*Handbook of Chemical Microscopy*, J. Wiley & Sons, New York, 1930, 1, 899) are preferred, especially where material is limited.

<sup>17</sup> S. P. Mulliken, *Identification of Pure Chemical Compounds*, 1st Ed., J. Wiley & Sons, New York, 1904, I, 10.

to any characteristic odors (such as acrolein indicative of glycerol or glycerides) which may be evolved. During fusion the odors typical of the various types of synthetic resins are especially strong and may be of assistance in identification. If aldehydes and phenols are present, they may be absorbed in water during destructive distillation of the resin.

Color tests for rosin with acetic anhydride and sulphuric acid, as in the Liebermann-Storch<sup>19</sup> procedure, may be confirmed by the Halphen-Hicks<sup>20</sup> method if desired. Many other color tests for rosin and other natural resins have been described. Brauer<sup>20</sup> and Fonrobert and Pistor<sup>21</sup> used phosphomolybdic acid, phosphotungstic acid or ammonium molybdate; Kämpf<sup>22</sup> has applied dilute copper acetate; Cohen<sup>23</sup> worked with chlorosulphonic acid in chloroform; and Griffon<sup>24</sup> added sulphuric acid to an alcohol solution containing the resin and furfural. Donath<sup>25</sup> suggested cooking the resin with concentrated nitric acid (sp.gr. 1.32-1.33) cooling, diluting and adding an excess of ammonia. Characteristic colors are given by various resins, that for rosin, for example, being orange which slowly changes to a deep brown-red.

Phthalates are identified by their reaction with resorcinol or phenol to give fluorescein or phenolphthalein, respectively.<sup>26</sup> Plasticizers derived from phthalic acid should be previously removed from the sample. The presence of phenols is confirmed by fusing the resin with caustic soda, acidifying, and applying the indophenol test.<sup>27</sup>

Several other tests have been proposed for the identification of phenols. In some instances coupling of the phenolic body with a diazonium compound yields dyes of characteristic colors. Phenol and diazotized p-nitroaniline give a rose-red dye, cresols furnish a rose-pink colored substance, and naphthols blue compounds.<sup>28</sup> Spectroscopic examination of the color is often helpful.<sup>29</sup> Zamparo<sup>30</sup> has described various color reactions given by resorcinol, phloroglucinol and  $\alpha$ - or  $\beta$ -naphthol with hydrogen peroxide in acid (sulphuric or hydrochloric) solutions. Other tests are based on the reaction of phenols with aldehydes, e.g., formaldehyde<sup>31</sup> or vanillin,<sup>32</sup> dihydroxyacetone,<sup>33</sup> and aromatic amines,<sup>34</sup> such as benzidine and toluidine.

<sup>19</sup> The Liebermann test (C. Liebermann, *Ber.*, 1884, 17, 1884) and derived methods are discussed and extended by W. A. LeLande, Jr., *J.A.C.S.*, 1933, 55, 1536. Modifications of the test (particularly for rosin dissolved in linseed oil) are given by J. J. Deeney, *Am. J. Pharm.*, 1932, 104, 282; *Chem. Abs.*, 1932, 26, 2330. For tests on resins and lacquers, see Z. Leppert and Z. Majewska, *Przemysł Chem.*, 1932, 16, 130; *Chem. Abs.*, 1932, 26, 6163; *Farben-Ztg.*, 1932, 38, 154; *Chem. Abs.*, 1933, 27, 615. A. Kraus (*Farben-Ztg.*, 1932, 38, 322; *Chem. Abs.*, 1933, 27, 856) finds distinctive colorations for various types of resins.

<sup>20</sup> E. F. Hicks, *Ind. Eng. Chem.*, 1911, 3, 86. Using phenol and bromine in carbon tetrachloride.

<sup>21</sup> K. Brauer, *Chem.-Ztg.*, 1926, 50, 371; *Chem. Abs.*, 1926, 20, 2755. This is known as the Brauer method.

<sup>22</sup> E. Fonrobert and K. Pistor, *Chem.-Ztg.*, 1927, 51, 139; *Chem. Abs.*, 1927, 21, 1716. The Storch-Morawski (acetic anhydride-sulphuric acid) test is preferred for rosin.

<sup>23</sup> P. Kämpf, *Pharm. Acta Helv.*, 1931, 6, 170; *Chem. Abs.*, 1932, 26, 3390. Identifies rosin from among 100 samples including many natural resins.

<sup>24</sup> H. C. Cohen, *Farben-Ztg.*, 1930, 36, 121; *Chem. Abs.*, 1931, 25, 222. Tung, linseed and stand oils do not interfere.

<sup>25</sup> H. Griffon, *J. Pharm. Chim.*, 1931, 14, 337; *Chem. Abs.*, 1932, 26, 2612.

<sup>26</sup> E. Donath, *Farben-Ztg.*, 1931, 36, 1176, 1473; *Chem. Abs.*, 1930, 24, 5515; *ibid.*, 1931, 25, 222. See also E. Stock, *Farben-Ztg.*, 1931, 36, 1176; *Brit. Chem. Abs. B*, 1931, 553.

<sup>27</sup> D. Cannegieter, *Verfakroniek*, 1934, 7, 256; *Chem. Abs.*, 1935, 29, 2003. Phthalic acid may be determined by heating the resin, condensing the vapors of phthalic anhydride and dissolving in hot water, and then titrating the acid solution.

<sup>28</sup> H. D. Gibbs, *J. Biol. Chem.*, 1927, 72, 649; *Chem. Abs.*, 1927, 21, 1946.

<sup>29</sup> J. Moir, *J. S. Afr. Chem. Inst.*, 1922, 5, 8; *Chem. Abs.*, 1922, 16, 1551.

<sup>30</sup> S. Palkin and H. Wales, *J.A.C.S.*, 1924, 46, 1488.

<sup>31</sup> A. Zamparo, *Boll. chim. farm.*, 1924, 63, 161; *J.S.C.I.*, 1924, 43, 445B; *Boll. chim. farm.*, 1925, 64, 97; *J.S.C.I.*, 1925, 44, 278B. A. H. Ware, *Quart. J. Pharm.*, 1929, 2, 267; *Brit. Chem. Abs. B*, 1929, 844.

<sup>32</sup> C. E. Sage and H. R. Flech, *Analyst*, 1932, 57, 567; *Chem. Abs.*, 1932, 26, 5513.

<sup>33</sup> A. H. Ware, *Quart. J. Pharm.*, 1929, 2, 249, 254; *Brit. Chem. Abs. B*, 1929, 844.

<sup>34</sup> A. H. Ware, *Quart. J. Pharm.*, 1929, 2, 267; *Brit. Chem. Abs. B*, 1929, 844.

<sup>35</sup> W. H. Bentley and B. Catalow, *British P.* 374,010, 1931, to W. Blythe & Sons, Ltd.; *Brit. Chem. Abs. B*, 1932, 833.

## QUANTITATIVE VALUES

Acid numbers<sup>35</sup> and saponification values should be determined. These often indicate the type of resin (under examination) and also the degree of condensation. Titration is usually carried out in a neutral ethyl alcohol or alcohol-benzene solution. Methods employing a two-layer system of benzene-alcohol and saturated aqueous sodium chloride solution are described by Stock<sup>36a</sup> and Coburn.<sup>36</sup> Good end-points are obtained with phenolphthalein, but Weinberger and Gardner<sup>37</sup> have shown that such methods give erroneous results for some resins, particularly shellac. An indirect method for acid number has been developed by Dieterich<sup>38</sup> whereby the resin is dissolved in a standard amount of alkali and then titrated with acid. This procedure is not applicable when easily saponified esters are present, and is unsatisfactory specifically for shellac. It is applicable, however, to many dark-colored resins.

One of the most accurate methods for the determination of acid numbers is electrometric or potentiometric titration and a type of cell for this purpose has been developed by LaMer and Downes.<sup>39</sup> However, no standard procedure has as yet been developed which is to be recommended for all resins.

According to Ulrich,<sup>40</sup> phthalic acid may be determined in the following manner: The sample (15-20 g.) is refluxed with benzene and excess 1*N* alcoholic potassium hydroxide for 4 hours. The mixture is then diluted with water, and alcohol and benzene removed by distillation. Any unsaponifiable matter is extracted with ether. The aqueous alkaline solution is acidified with hydrochloric acid and monocarboxylic acids separated with benzene (in which they are soluble). The residue is made just alkaline with sodium hydroxide and lead acetate added. The precipitate of lead phthalate is washed with dilute acetic acid and converted to lead sulphate.

Saponification numbers can be determined by heating a weighed sample of resin with 0.5*N* or 1*N* sodium hydroxide in methanol and titrating the excess alkali.<sup>41</sup> Equal volumes of benzene and normal alcoholic caustic may be employed when the resin is difficultly soluble.<sup>42</sup> The usual indicator is phenolphthalein, though others may be employed. Salvaterra<sup>43</sup> has proposed alkali blue as an indicator in titrating resins which give dark colored solutions.

In cases of high saponification numbers it may be desirable to treat enough material so that the acids can be identified, since a number over 200 is a strong indication of esters of the polybasic acid type. Wolff<sup>44</sup> has used a variation of the Twitchell method to separate oxidized fatty acids and resin acids by means of diethyl sulphate. Acid, saponification and iodine numbers may be determined on

<sup>35</sup> A review of acid number determinations has been given by H. Weinberger and W. H. Gardner (*Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 267). E. W. Diener and S. Werthan (*Proc. Am. Soc. Testing Materials*, 1908, 98; *Chem. Abs.*, 1930, 24, 3916) give a method for use on driers and soaps when metals are present. L. Hambrook (*J.S.C.I.*, 1927, 5, 147) has cited an example of the use of acid numbers as applied to copal varnish.

<sup>36a</sup> E. Stock, *Farben-Ztg.*, 1929, 34, 1727; *Chem. Abs.*, 1929, 23, 3359

<sup>36</sup> H. H. Coburn, *Ind. Eng. Chem., Anal. Ed.*, 1930, 2, 181.

<sup>37</sup> H. Weinberger and W. H. Gardner, *loc. cit.*

<sup>38</sup> K. Dieterich, "Analyse der Harze, Balsame und Gummi-Harze," Julius Springer, Berlin, 1930. Compare also the modification used by R. A. Worstall, *J.A.C.S.*, 1903, 25, 862.

<sup>39</sup> V. K. LaMer and H. C. Downes, *J.A.C.S.*, 1933, 55, 1840.

<sup>40</sup> H. Ulrich, *Farbe u. Lack*, 1934, 318; *Chem. Abs.*, 1935, 29, 2257.

<sup>41</sup> H. A. Gardner ("Physical and Chemical Examination of Paints, Varnishes and Lacquers," *loc. cit.*) recommended 0.2*N* potassium hydroxide in absolute methanol.

<sup>42</sup> T. F. Bradley, *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 304.

<sup>43</sup> H. Salvaterra, *Chem.-Ztg.*, 1919, 43, 765; *Chem. Abs.*, 1920, 14, 642. Another method involves adding barium chloride to the alkaline solution after saponification of the resin. Barium resins are precipitated leaving a clear solution to be titrated with acid.

<sup>44</sup> H. Wolff, *Chem. Umschau*, 1924, 31, 87; *J.S.C.I.*, 1924, 43, 525B.

the separated material. The Wijs method<sup>45</sup> has been recommended for iodine number, both on the acids and on the original resin.

### SPECIALIZED EXAMINATIONS

Various other constants, such as ester value, Helmer's number, acetyl value, Maumené number, Reichert and Reichert-Meissel value and hydroxyl number<sup>46</sup> have been used in the identification of oils, fats and waxes and some may occasionally be applied advantageously to resins. Cumaron-indene resins may be identified by the methods of Wolff as modified and extended by Ellis.<sup>47</sup>

Special chemical tests are made on resins and resin products to determine certain definite properties. The solubility of many commercial resins in various solvents has been reported by Van Heuckeroth<sup>48</sup> while Ostwald and Gamm<sup>49</sup> studied the solubilities of both natural and synthetic resins in sodium hydroxide solutions.

Certain resins may be identified according to a method known as capillary analysis developed by Stock<sup>50</sup> and described by Fonrobert and Pistor.<sup>51</sup> It is based on the observation that pieces of filter paper, partially immersed in resin solutions for periods up to 24 hours, show variations in capillary rise, color, opacity and general appearance which, under controlled conditions, may be sufficiently characteristic for classification.

Analyses may be conducted on resin products for special information. For example, resins can be ashed and the residue examined for traces of lime, soda, or other material which might have been used as a catalyst. Confirmatory tests may be applied for lubricants such as stearic acid, mineral oil or carnauba wax. Mineral fillers are readily determined, in most cases both qualitatively and quantitatively, and in some cases a fineness test on the filler, by screen analysis or microscopic examination, is worth while. Organic or carbonaceous fillers such as wood flour, cotton flock, carbon black, graphite, or lampblack are more difficult, as they do not show up on ashing the sample. Microscopic examination of a broken surface and of the ash will be helpful in some instances. Bone black in appreciable quantity can be detected by an analysis of the ash for phosphate, which is especially significant if calcium is also found to be present.

Plasticizers may be separated and determined in the case of coating materials tested before application and sometimes in thermoplastic preparations, such as cellulose-ester-base plastics, vinyl and styrene resins, shellac and other natural resins. In this respect, inspections of articles molded from reactive resins are difficult, but unreacted molding powders should yield some information. Ryan

<sup>45</sup> J. J. A. Wijs, *Analyst*, 1929, 54, 12; *Chem. Abs.*, 1929, 23, 1518. Also J. J. A. Wijs, *Chimie et industrie*, 1928, 20, 1043; *Chem. Abs.*, 1929, 23, 2052.

<sup>46</sup> W. L. Roberts and H. A. Schuette, *Ind. Eng. Chem., Anal. Ed.*, 1932, 4, 257.

<sup>47</sup> A rapid method for determining the presence of cumaron is by a color reaction with bromine. Cumaron resins will give a permanently red color when treated with bromine in a solution of dry chloroform in the presence of glacial acetic acid. Pontianac will color the solution yellow though there may be a slight red tint when the bromine is first added. It is therefore advisable to check the color after the solution has stood for some time, usually 24 hours. Often one hour's time is sufficient to develop the color definitely except when Pontianac resin is present in large proportions, and in this case it is preferable to resort to the destructive distillation of the resin with the subsequent identification of cumaron and indene in the distillate as given above.

The test is carried out as follows: 1 cc. of a 10 per cent solution of the resin in chloroform is diluted with 6 cc. of chloroform and 1 cc. of glacial acetic acid is added. The solution is then shaken or stirred and 1 cc. of a 10 per cent solution of bromine in chloroform is added, the solution again shaken or stirred, the container corked and allowed to stand, the presence of cumaron resin being indicated by the permanent red color of the solution.

The foregoing method of separating and identifying cumaron resin was developed and successfully used in the author's laboratory.

<sup>48</sup> A. W. Van Heuckeroth, *Circ. Am. Paint, Varnish Mfrs. Assoc.*, 1930, 369, 354.

<sup>49</sup> W. Ostwald and W. Gamm, *Kolloid-Z.*, 1933, 62, 324; *Chem. Abs.*, 1933, 27, 2317.

<sup>50</sup> E. Stock, *Farben-Ztg.*, 1926, 31, 1903, 1959, 2133, 2187, 2240; *Chem. Abs.*, 1927, 21, 1717.

<sup>51</sup> E. Fonrobert and K. Pistor, *Farben-Ztg.*, 1927, 32, 2424; *Brit. Chem. Abs. B*, 1927, 661.

and Watkins<sup>55</sup> have given procedures for the determination of plasticizers in cellulose ester compositions.

Solvents for resins and cellulose derivatives are becoming so numerous and complex that they can no longer be detected by their odor and, perhaps, boiling range. A recognized procedure, moreover, is not available and identification has to be made by fractional distillation, boiling range, density, and optical properties, confirmed by special tests if necessary. Jordan<sup>56</sup> has given much information which is of value in the examination of both solvents and plasticizers. Gardner<sup>57</sup> and Durrans<sup>58</sup> also collected considerable data on both subjects.<sup>59</sup>

#### APPEARANCE, COLOR AND OPTICAL PROPERTIES OF RESINS

Bradley<sup>57</sup> has based his scheme of analysis on the density and refractive index of the various resins, but certain investigators have taken advantage of other optical properties for identification. Stock<sup>60</sup> and Nicolardot and Coffignier<sup>61</sup> have reported that they are able to distinguish various resins and also show why some gums are brittle merely by visual examination under the microscope. Adulteration and uniformity of blended products may also be observed. Roninger<sup>62</sup> described microscopic methods employed for rubber, but requiring only little variation for use on resins or their products.

Any polarizing action of the resin may of course be observed between crossed Nicol prisms in a microscope equipped for this purpose and may be conveniently investigated when the refractive index is measured.

The color and color-stability is of importance, especially in the field of coatings and light-colored molded and turnery products. Van Heuckeroth<sup>63</sup> has reported initial color estimates on resins used in coatings, and also stated the extent to which the film darkened on exposure. A number of instruments are now available which will determine and record the color of opaque objects as a graph of the spectrum showing the intensity of the light of each different color. Investigations of resins are usually made by transmitted light, however, and are not so complete. As a basis of comparison, Fonrobert<sup>62</sup> suggested a solution of iodine in potassium iodide and gave numerical values corresponding to the rosin color standards.<sup>63</sup> Albert<sup>64</sup> advocated solutions of potassium chromate or dichromate.

The value of the refractive index as a means of classification has been pointed out, but considerable care must be taken in making observations as the results may be influenced by particle size, reflectivity and other factors, including water.<sup>65</sup> Plonait<sup>66</sup> employed optical rotation of solutions to distinguish real amber from copal resins and to detect adulterations. Double refraction due to the "streaming" effect of rod-like molecules has been noted in colloidal solutions of many highly

<sup>55</sup> J. D. Ryan and G. B. Watkins, *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 191.

<sup>56</sup> O. Jordan, "Chemische Technologie der Lösungsmittel," Julius Springer, Berlin, 1932.

<sup>57</sup> H. A. Gardner, "Physical and Chemical Examination of Paints, Varnish and Lacquers," 5th Ed., Inst. Paint & Varnish Research, Washington, D. C., 1930.

<sup>58</sup> T. H. Durrans, "Solvents," 2nd Ed., Chapman & Hall, Ltd., London, 1931.

<sup>59</sup> The kauri-butanol test, designed to predict the value of a solvent as a varnish or lacquer thinner, is described in Chapter 70.

<sup>60</sup> T. F. Bradley, *loc. cit.*

<sup>61</sup> E. Stock, *Farben-Ztg.*, 1925, 30, 2340, 2407, 2475, 2542, 2604, 2668; *Chem. Abs.*, 1925, 19, 3026.

<sup>62</sup> P. Nicolardot and C. Coffignier, *Chimie et industrie*, 1924, 11, 456; *Chem. Abs.*, 1924, 18, 1915.

<sup>63</sup> F. H. Roninger, Jr., *Ind. Eng. Chem., Anal. Ed.*, 1933, 5, 251.

<sup>64</sup> A. W. Van Heuckeroth, *Circ., Am. Paint & Varnish Mfrs. Assoc.*, 1930, 369, 354.

<sup>65</sup> E. Fonrobert, *Farben-Ztg.*, 1925, 30, 3057; *Chem. Abs.*, 1926, 20, 117.

<sup>66</sup> The Hellige-Stock-Fonrobert color comparator is now available, employing colored glass discs rather than liquids, suitable for either solutions or solids. See also E. Fonrobert, *Farben-Ztg.*, 1932, 37, 1320; *Chem. Abs.*, 1932, 26, 4724; *Paint Mfr.*, 1933, 3, 10, 21; *Chem. Abs.*, 1933, 27, 1526.

<sup>67</sup> K. Albert, *Farben-Ztg.*, 1924, 29, 576; *Chem. Abs.*, 1925, 19, 185.

<sup>68</sup> C. Cheneveau, *Compt. rend.*, 1925, 180, 1105; *Chem. Abs.*, 1925, 19, 1809.

<sup>69</sup> C. Plonait, *Chem. Umschau Fette, Oele, Wachse, Harze*, 1930, 37, 344; *Chem. Abs.*, 1931, 25, 1107.

polymerized compounds by Signer.<sup>67</sup> X-Rays have been used extensively<sup>68</sup> in the study of the structure of both natural and artificially polymerized colloids<sup>69</sup> and Ott<sup>70</sup> has reported the degree of polymerization of certain aldehydes by means of this type of measurement.

Phenol-formaldehyde resins are transparent to ultraviolet rays to a depth of 0.7 mm. with resultant yellowing, according to Risler.<sup>71</sup> Clement, Riviere and Beck<sup>72</sup> found that pure nitrocellulose is not darkened by ultraviolet light, but that traces of phenolic compounds do bring about this change. Sugimoto and Kasai<sup>73</sup> studied light absorption and transmission by phenol-formaldehyde resins in both visible and ultraviolet light. When no condensing agent was used, broad absorption bands were produced in the ultraviolet range. These were shifted by the addition of various amounts of a transparent lemon-yellow resinous decomposition product of hexamethylenetetraminetriphenol, the latter being formed when ammonia was used as a condensation agent in the original reaction.

Distinguishing fluorescent effects have been noted when resins are exposed to ultraviolet rays. Wolff and Toeldte<sup>74</sup> have given tables showing the characteristic color and appearance of the fluorescence when resins were examined in the form of lumps, powder or solutions in butyl acetate.<sup>75</sup> Danckwortt<sup>76</sup> has discussed the use of ultraviolet fluorescence in the examination of resins and also solvents, oils, various pigments and driers.

#### HEATING AND TEMPERATURE EFFECTS ON RESINS

The colloidal nature of both synthetic and natural resins is apparent from their behavior when heated, as they usually do not exhibit a clearly defined melting point.<sup>77</sup> The properties change gradually, sometimes over a very wide range of temperature, while the specific heats are complicated by heats of transformation from one form to another which furthermore may occur at different points on heating and on cooling. In the case of certain reactive resins these changes are not reversible, as curing may take place below the melting point of the resin. Plasticizers or solvents may affect softening points and not the reaction temperatures, while hardening agents or condensing agents often alter the reaction temperature alone.

Many different methods have been proposed for the determination of the softening and melting points of resins and similar materials.<sup>78</sup> Van Heuckeroth<sup>79</sup>

<sup>67</sup> R. Signer, *Z. physik. Chem.*, 1930, 150, 257; *Chem. Abs.*, 1931, 25, 449.

<sup>68</sup> G. L. Clark, "Applied X-Rays," 2nd Ed., McGraw-Hill Book Co., New York, 1933.

<sup>69</sup> See Chapter 4 for discussion of the application of x-rays in the field of synthetic resins.

<sup>70</sup> E. Ott, *Z. physik. Chem.*, 1930, 9, 378; *Chem. Abs.*, 1930, 24, 5554. *Science*, 1930, 71, 465; *Brit. Chem. Abs. A*, 1930, 1098.

<sup>71</sup> J. Risler, *Compt. rend.*, 1925, 181, 782; *Chem. Abs.*, 1926, 20, 710.

<sup>72</sup> L. Clement, C. Riviere and A. Beck, *Chimie et industrie, Special No.*, March 1932, 27, 702; *Chem. Abs.*, 1932, 26, 3662.

<sup>73</sup> S. Sugimoto and E. Kasai, *Reports Imp. Ind. Research Inst. Osaka, Japan*, 1927, 7 (14), 1; *Chem. Abs.*, 1927, 21, 2172.

<sup>74</sup> H. Wolff and W. Toeldte, *Farben-Ztg.*, 1926, 31, 2503; *Chem. Abs.*, 1927, 21, 2806.

<sup>75</sup> Albertol resins show the most intense color (blue) while ester gum, lime-hardened rosin and Congo copal in decreasing intensity show blue. G. Kostka (*Chem. Ztg.*, 1920, 53, 117, 138; *Chem. Abs.*, 1920, 23, 2308) has reported that phenol-formaldehyde resins do not fluoresce although they absorb the ultraviolet light. Amber is indicated by a yellow-green to blue-white color, but the pressed and cloudy forms are less active. Urea-formaldehyde resins exhibit a faint fluorescence, casein and cellulose products show blue or blue-white, and all are easily distinguished from amber. Filters are available which pass the ultraviolet but restrict all other rays, including visible light.

<sup>76</sup> P. W. Danckwortt, *Farben-Chem.*, 1932, 3, 140; *Brit. Chem. Abs. B*, 1932, 613.

<sup>77</sup> Crystalloids absorb heat at a more or less uniform rate corresponding to the specific heat of the solid. Then melting occurs, and the heat of fusion is absorbed at a temperature which, for pure substances, does not vary a fraction of a degree. When all the solid has melted more heat raises the temperature of the liquid at a new rate corresponding to the different and usually higher specific heat of the liquid. Temperatures are sharp and heat effects may readily be measured.

<sup>78</sup> H. A. Gardner, "Physical and Chemical Examination of Paints, Varnish and Lacquers," 5th Ed., Inst. Paint & Varnish Research, Washington, D. C. H. Abraham, "Asphalt and Allied Substances," 2nd Ed., D. Van Nostrand Co., New York, 1920.

<sup>79</sup> A. W. Van Heuckeroth, *Circ., Amer. Paint & Varnish Mfrs. Assn.*, 1930, 369, 354.

has compiled the softening points of commercial soluble synthetic resins available in the United States. Nagel<sup>60</sup> has reported values for German resins using a modification of the Krämer-Sarnow mercury method. In the Durrans procedure,<sup>61</sup> 3 g. of the resin (in a test tube) are carefully melted, and the mass allowed to cool and harden. Fifty g. of mercury are placed on the solid and the container and contents slowly heated (2°C. per min.) The temperature at which the resin floats on the mercury is taken as the melting point. This method has been modified by Rangaswami<sup>62</sup> for use with small amounts (0.2 g.) of material. While no system has been accepted for general use, the American Society for Testing Materials has issued tentative specifications for the determination of the softening and fluid temperatures of rosin.<sup>63</sup>

Melting points have been measured by Dennis and Shelton<sup>64</sup> using a long copper bar 1½" square, heated electrically at one end so that the temperature varies uniformly over the length of the piece. The material is placed on the top surface as a long trail of powder, and the degree of heat where melting is observed may be found by a sliding thermocouple. This device is well suited for work with resins, as the sample can be exposed simultaneously to a range of temperatures and the melting points or ranges noted. The effect of time on contact may also be found, and, with reactive resins, the curing may be observed, although the time is not comparable to that required when pressure is exerted on the specimen.

### VISCOSITY OF RESINS

The viscosity of resins is of practical importance in connection with coating and impregnating solutions.<sup>65</sup> Several of the viscometers<sup>66</sup> developed primarily for the oil industry may be adapted to this work but comparative tests may be made with a pipette, or bubble tubes. Van Heuckeroth<sup>67</sup> has given the viscosity ranges of many varnish resins and Keyssner<sup>68</sup> has described the effect of the chemical constitution of the solvent on the viscosity of resin solutions.

### PHYSICAL AND ELECTRICAL TESTS ON RESINS

For purposes of identification, the physical and electrical characteristics of resins are of little value, although they have considerable significance from a commercial standpoint. However, in cases where this information may be required for the proper control of production, the apparatus and procedure will generally be found to be identical with those described for molding and coating preparations.<sup>69</sup>

<sup>60</sup> W. Nagel, *Wiss. Veröff. Siemens-Konz.*, 1925, 4, 321; *Brit. Chem. Abs. B*, 1926, 333. *Farben-Ztg.*, 1926, 31, 1627; *Chem. Abs.*, 1926, 20, 2419.

<sup>61</sup> T. H. Durrans, *J. Oil Colour Chem. Assn.*, 1929, 12, 173; *Chem. Abs.*, 1929, 23, 4355.

<sup>62</sup> M. Rangaswami, *J. Oil Colour Chem. Assn.*, 1930, 13, 287; *Brit. Chem. Abs. B*, 1931, 34.

<sup>63</sup> F. P. Veitsch, et al., Report of Committee D-17 on Naval Stores. *Proc. Amer. Soc. Test. Mat.*, 1928, I, 602.

<sup>64</sup> L. M. Dennis and R. S. Shelton, *J.A.C.S.*, 1930, 52, 3128.

<sup>65</sup> Methods for the determination of viscosity of varnishes and lacquers are given in Chapter 70. The testing of plasticity of molding preparations is described in Chapter 69.

<sup>66</sup> H. A. Gardner, *loc. cit.*

<sup>67</sup> A. W. Van Heuckeroth, *loc. cit.*

<sup>68</sup> E. Keyssner, *Z. angew. Chem.*, 1926, 39, 99; *Brit. Chem. Abs. B*, 1926, 248.

<sup>69</sup> Methods for the determination of power factor, dielectric constant, electrical resistivity, hardness, tensile strength and water-resistance will be found in Chapters 69 and 70.



## Chapter 65

### Preparation of Hot-Molding Compositions

Synthetic resins are widely used as binders for molding compositions which are shaped under heat and pressure into a great variety of products. This application is an art in itself, and, as a result of continuing development is attracting increasing attention from designers, engineers, and artists, as well as from manufacturers in many fields.

Variations in molding properties and requirements, and the almost infinite number of shapes and applications of molded pieces, make it impossible to lay down fixed rules for manufacture, design of molds or manner of molding. Each resin, molding composition and product presents in some respects a distinct and separate problem, but information concerning present methods should be helpful in meeting new situations.

#### USES

The applications of thermoplastic molded products cover a large and diverse field. Compositions containing natural resins, such as shellac, are limited because of their poor resistance to heat but find extensive use in phonograph records and other articles that are not required to withstand elevated temperatures. Synthetic thermoplastic substances which are tough and have a higher softening point, for example the vinyl resins and certain resinous materials derived from rubber, are being used for many purposes, since they will stand more heat, but for extreme thermal resistance the thermosetting and cold-molded compositions are required.

Many thermosetting synthetic resins have been developed in recent years, typical of which are the urea resins, which are particularly useful because they combine light-stability with high mechanical strength and other physical properties required in this type of material. The alkyd resins are likewise being used in a number of special applications. There has been a tendency to employ various resins in the production of certain articles formerly made from rubber.<sup>1</sup>

It is often possible to substitute molded parts for metal, eliminating elaborate machine operations, with a consequent saving in cost and improvement in both appearance and service of the product. Not only may these plastic compositions be shaped as required,<sup>2</sup> with holes, screw threads, figures, letters and designs, but pieces of metal, rubber or other material may be wholly or partially embedded in the article at the time of molding, according to the requirements. The molded piece can also be obtained with a high surface luster that needs little or no finishing treatment, allowing the article to be completed in all respects in a single molding operation. The process adapts itself readily to mass production at low unit cost by the use of multiple-cavity molds and modern presses.

The electrical properties of most resinous compositions are excellent, so that

<sup>1</sup> F. Cellin, *Metallbörse*, 1935, 24, 1417, 1482; *Chem. Abs.*, 1935, 29, 2026.

<sup>2</sup> J. Scheiber and K. Sändig ("Artificial Resins," Trans. by Fyleman, Pitman, London, 1931, 362) have given a list of over 200 articles made from phenol-formaldehyde resins. The products range from acid-proof coatings to x-ray tubes, and include such diverse items as pistons, necklaces, sword handles, banjo frames and pipe line. The list was furnished by Bakelite G.m.b.H.

molded articles may be advantageously employed in electrical apparatus and instruments of many types.<sup>a</sup> Metal inserts may serve as contacts or conductors as well as for purely mechanical purposes. Molding compositions which transmit electricity to some extent may result when large proportions of graphite, copper powder or other powdered conductors are incorporated. By proper proportioning, such mixtures may be used as resistors, for example in radio work.

The ability of some molding materials to become quite plastic and flow readily under pressure when heated permits the forming of articles with thin strong walls, an important advantage in many diversified uses particularly where light weight in relation to size is a factor. Products molded with heat-resistant compositions will retain their shape and color at elevated temperatures and find many applications in connection with electrical heating appliances.

These preparations are likewise adapted for ornamental and decorative purposes, because of the lustrous finish obtained by the use of a highly polished mold. Smokers' articles, boudoir and toilet accessories, boxes and bottle closures may be taken as examples. Compositions of either uniform or mottled colors afford a wide choice for artistic development.

### MOLDING PROCESSES AND COMPOSITIONS

In the actual molding operation the composition of resin and non-resinous fillers is given the desired form by use of some kind of a mold together with heat, pressure, chemical reaction, evaporation, cooling, or some combination of these.<sup>4</sup> The permanently thermoplastic materials are heated, placed in the mold under pressure and hardened by cooling. Necessarily, thermoreactive resins are thermoplastic in the first stages of pressing and are given the required shape while in this state, followed by hardening due to chemical reaction, usually produced by further heating in the mold, so that the shaped article may be removed from the press with little or no cooling. These compositions for thermoplastic and for thermoreactive molding are mixtures of the desired natural or synthetic resins with fibrous materials, powdered fillers, dyes, pigments, lubricants and sometimes plasticizers. They are hard at ordinary temperatures, and may be used in the form of sheets, powder or compressed pellets or pills. In cold molding, a soft, powdered material is shaped at room temperature under very high pressures to form an article which must then be hardened outside of the mold by evaporation of any solvent and baking at relatively high heat.<sup>5</sup>

### RANGE OF PROPERTIES AVAILABLE

The increasing demands of industry for molded articles to meet specific needs has made available a number of compositions possessing various combinations of properties.<sup>6</sup> These characteristics may be varied within certain limits and can be utilized to advantage in meeting the particular requirements imposed by the shape and size of the piece and the service demanded of it.

The properties of moldings made with the same composition vary so widely as to prevent the presentation of precise data which will be generally applicable. For example, the length of time that a particular piece made with a reactive binder is heated under pressure is of fundamental importance in fixing its char-

<sup>a</sup> L. E. Barringer, *Gen. Elec. Rev.*, 1927, 30, 387. W. W. Werring, *Bell. Lab. Record*, 1931, 9, 470; *Chem. Abs.*, 1931, 25, 4071. J. A. Crabtree, *British P.* 344,422, 1929; *Chem. Abs.*, 1932, 26, 3312.

<sup>4</sup> A large number of variations are possible when so many factors are involved but the more important methods of molding actually in use are described in Chapter 68.

<sup>5</sup> The subject of cold molding is treated in Chapter 66.

<sup>6</sup> K. Ripper, *Plastics*, 1930, 6, 384; 402; *Chem. Abs.*, 1930, 24, 4342.

acteristics. From the standpoint of production, the period of cure influences the proper ejection of the molded article from the mold, and subsequent satisfactory service is likewise to a great extent dependent upon correct treatment in this stage. Under-cured pieces, while seemingly perfect on the surface, may distort with temperature changes, are susceptible to atmospheric conditions and are more readily affected by moisture and solvents than properly finished products.

Molding compositions containing reactive resinous binders may be so processed by the manufacturer as to have different degrees of plasticity and are usually available in three grades, soft, medium and hard. This allows the choice of the type giving the correct flow under the particular conditions employed, resulting in more uniform cure and better quality. Mixtures or blends of different hardness may be used if closer regulation is desired.

In addition to their value as electrical insulators and their ability to resist high temperatures, other properties of thermosetting compositions have promoted their extensive use in articles which must be unaffected by weather conditions, moisture, chemicals, acid fumes and solvents. The molded material can be machined and finished to a smooth surface, or it may be drilled and tapped, forming a substantial thread. A few unusual applications will illustrate the variety of uses of the products. Storage battery boxes may be molded in one operation,<sup>7</sup> scale cases<sup>8</sup> and radio cabinets may be made in complicated and attractive shapes, sizes and colors. Balance weights show small change due to wear because of the low specific gravity of the material as compared to metal. Water faucets<sup>9</sup> are now molded and, of course, are free from corrosion.

The unusual resistance to wear is responsible for a great number of applications as in floor coverings,<sup>10</sup> brake lining compositions<sup>11</sup> and even bearings; also the notable waterproofing action is of value in general service as well as for electrical equipment.

Various methods of decoration have been described which are particularly adapted to synthetic plastic materials;<sup>12</sup> for example, openwork patterns<sup>13</sup> or metal powder<sup>14</sup> may be molded into the surface of an article.

**Color.** Synthetic resin products are made in all colors,<sup>15</sup> but not every type of composition affords variety in this respect. Molding materials containing urea resins as binders can be secured in practically all colors from black to white with perfect stability to light. Such preparations are generally molded at a slightly lower temperature than those using a phenolic resin binder. Translucent articles in various shades can also be obtained from urea resins and these are being used to a considerable extent in commercial art.

The alkyd resins are also available in the lighter colors. However, they have the disadvantage of requiring a much longer curing time and their application is therefore confined largely to casting rather than rapid press molding.

Plastic phenolic compositions are made in several colors, black and brown being most widely used. Red, green and blue are also prepared but pastel shades and white are difficult to produce and maintain because of the effect of light on

<sup>7</sup> G. W. Bulley, U. S. P. 1,566,815, Dec. 22, 1925; *Chem. Abs.*, 1926, 20, 530. *British Plastics*, 1933, 5, 438, 450, 451.

<sup>8</sup> C. F. M. van Berkel, *British P.* 338,424, 1930; *Chem. Abs.*, 1931, 25, 2312.

<sup>9</sup> See *British Plastics*, 1931, 3, 197.

<sup>10</sup> D. L. Irwin and R. E. Tipples, *British P.* 345,386, 1930; *Chem. Abs.*, 1933, 27, 616. W. F. Kaufman and J. C. McCarthy, *British P.* 347,527, 1929, to Armstrong Cork Co.; *Chem. Abs.*, 1933, 27, 616. F. Hayer, *Kunststoffe*, 1933, 23, 61; *Chem. Abs.*, 1933, 27, 2317.

<sup>11</sup> J. N. Loughley, *British P.* 376,386, 1931, to Ferodo, Ltd.; *Brit. Chem. Abs. B*, 1932, 1013.

<sup>12</sup> G. Payras, *Rev. gen. mat. plastiques*, 1929, 5, 655; *Chem. Abs.*, 1930, 24, 4360. R. Houwink, *Ingenieur (Holland)*, 1932, 47, W101; *Chem. Abs.*, 1933, 27, 2317.

<sup>13</sup> E. A. Stubbs, *British P.* 280,017, 1926; *Chem. Abs.*, 1928, 22, 3056.

<sup>14</sup> J. Eaton, *British P.* 301,432, 1927, to British Thompson-Houston Co., Ltd.; *Brit. Chem. Abs. B*, 1930, 781. See also R. Schwarz, *German P.* 605,716, 1934; *Chem. Abs.*, 1935, 29, 1905.

<sup>15</sup> A. J. Steinberger, *Plastics and Molded Prod.*, 1933, 8, 278.

the phenolic resin. Excessive temperature or length of heating in manufacture will also cause darkening.<sup>10</sup>

For many purposes, such as containers for toilet preparations and foods, it is of the utmost importance that the molded product retain its color without leaching or bleeding, to avoid discoloration of the contents. As such articles are likely



*Courtesy Bakelite Corp.*

FIG. 168.—Matching Colors of Polystyrene on Laboratory Rolls.

to be used in contact with many substances whose compositions are unpredictable and often a trade secret, it is impossible to give any fixed rule of color selection that will cover all contingencies. It is advisable when there is any doubt regarding the effect of a substance on the color selected, to make an actual test before starting a production schedule.

Cast phenolic resins are available in great variety ranging from opaque to translucent or transparent. They are somewhat susceptible to light, but are finding wide use for cutlery handles, jewelry, clock cases, lamps, and many other small ornamental objects.

<sup>10</sup> R. Jones, *British Plastics*, 1933, 4, 538; 5, 20. This discusses dyes and pigments, and discoloring of both resins and colors under various conditions.

The vinyl and styrene resins are also used in color work to advantage as they are transparent or translucent and do not darken when exposed to light. Numerous colored objects made of vinyl resin compositions have been described by Davidson and McClure,<sup>17</sup> including wall panels, cosmetic jars, dentures, phonograph records<sup>18</sup> and automobile steering wheels. See Fig. 168.

**Surface Finish.** The smooth, lustrous surface on a molded article is primarily dependent on the finish of the mold. Most of the molded products that are used for artistic purposes are hot-pressed and the high initial luster is permanently retained by high grade material of this type. Gloss may be further increased by a light burnishing, as with a soft rag buffing wheel, but care is required that the surface resin is not removed from the article by this operation.

The finish may, however, be injured by molding conditions. Excessive temperature is apt to cause waviness, and too rapid closing of the mold before the material is sufficiently plastic may result in flow marks. Delay in closing a hot mold after a reactive composition has been placed in it will produce dull lusterless patches as a result of the reaction of the resinous binder without pressure.

Insulators formed in a highly polished mold will have better permanent electrical surface resistivity than those made in a poorly polished mold, as a film of dirt or moisture will form more readily on a dull or uneven area.

The proportion of resinous binder in the composition is also an important factor in obtaining a lustrous finish. High polish is secured by forming a surface layer of practically clear resin produced by the pressure of molding which compacts the mass and forces excess binder to the outside. Preparations deficient in resin will produce unattractive pieces.

**Mechanical Strength.** The mechanical strength of molded products is of the utmost importance in a majority of applications, the main factor being the ability to resist shock. The strength of most molded compositions against impact lies partly in the quantity and fibrous nature of the filler. Examples of manufacturing conditions which may reduce the mechanical strength of an otherwise satisfactory article are a temperature too low to flux the binder properly, pressure insufficient to compact the material, the use of a composition which has too little plasticity to fill the mold completely, and charging too small an amount of material when employing a semi-positive mold.

For most purposes, preparations containing wood flour filler have sufficient strength. Materials that have a relatively high resistance to shock are also available and are composed of a long-fibrous filler or small pieces of fabric combined with a resinous binder. Long-fiber asbestos is used particularly when the molded article is required to resist the disintegrating effect of high temperature or acids.

**Heat Resistance.** Heat resistance<sup>19</sup> of molded products is, for many purposes, quite as important as mechanical strength and always requires consideration. Articles that will not withstand a temperature of 100°F. (38°C.) without deformation are suitable only for use in temperate climates and care is needed to see that they are not exposed to direct sunlight. Compositions containing a permanently fusible, low-melting binder, shellac for instance, will warp and become distorted by the heat of the sun or even at moderate room temperatures when subjected to some pressure. Thermoplastic materials of higher melting point such as vinyl or styrene resins and certain resins

<sup>17</sup> J. G. Davidson and H. B. McClure, *Ind. Eng. Chem.*, 1933, 25, 645; *Plastic Products*, 1933, 9, 143.

<sup>18</sup> H. Chase, *British Plastics*, 1933, 4, 446. A thermoplastic compound made from rubber is available from deep to pastel shades and may be transparent or opaque. The resin itself is a light amber color and is not affected by light.

<sup>19</sup> For method of measurement see Chapter 69.

derived from rubber, will stand considerable exposure to heat especially when highly filled, but molding compositions containing a reactive resin as a binder, when properly treated for conversion to the infusible state, are unaffected by much higher temperatures. Phenol-formaldehyde moldings containing wood fillers are not damaged by a continuous temperature of 250°F. (125°C.) under conditions of normal humidity, while products containing an asbestos filler may be heat-resistant for short periods up to 570°F. (300°C.). Some of the latter have been satisfactorily used in contact with moisture in valve discs for steam lines and in acid-resistant ware for chemical plant equipment.

**Electrical Properties.** The American Society for Testing Materials and the National Bureau of Standards have made careful studies of the dielectric and mechanical properties of molded materials,<sup>20</sup> and methods of evaluation have been developed. As large quantities of molded products are used in electrical appliances and for insulation, the manufacturers of these compositions carefully guard against any reduction in dielectric value, avoiding contamination from metal or other conductive materials. Large quantities of such carefully made moldings have been satisfactorily employed for high-tension work.

These compositions are likewise well suited for use with the high-frequency currents encountered in the radio field. Groff has developed a preparation said to be highly resistant to surface leakage or arcing when properly molded.<sup>21</sup>

**Machining Characteristics.** In spite of the fact that synthetic plastic materials can be molded or cast in almost any form desired, there is considerable demand for products made by machining. The cast resins may be worked either automatically or by hand to produce finished articles from the rough shapes.

Molded articles usually are so designed that little machine work is required, unless it is on metal inserts as in the case of automobile distributor caps. The "flash" or overflow should not require any tooling for removal unless it be with a file or a punch. Occasionally, however, it is found more economical to drill or tap holes which would otherwise require a very complicated mold or press arrangement.

Laminated products made in sheet form are frequently punched, milled or otherwise fabricated to produce gears, wheels, or insulation. In general, standard tools may be used on all molded products, and machine shop practice is somewhat similar to that used for working brass.<sup>22</sup> Cutting edges dull very quickly, however, probably because the poor heat conductivity of the material creates unusually high temperatures, destroying the temper of the instruments.

Specially designed tools have been made for use on Bakelite and are recommended by some manufacturers when high-speed production is required. Tungsten carbide or diamond-pointed<sup>23</sup> implements have also been employed.

Punching dies are very similar to those used for metal, except that smaller clearance is required. The holes in the stripper plate should also be a close fit around the punch to prevent lifting the edge.

The sheeting or shaping operation, long used in cutting celluloid, has been applied to cast resins.<sup>24, 25</sup> When formed in lead molds they have been sliced into sheets by cutting both the mold and the resin at the same time.<sup>26</sup>

<sup>20</sup> For a description of testing procedure see Chapter 69.

<sup>21</sup> F. Groff, British P. 354,166, 1929, to Bakelite Corp.; *Brit. Chem. Abs. B*, 1931, 934. Canadian P. 309,679, 1931; *Chem. Abs.*, 1931, 25, 3138. French P. 689,126, 1930; *Chem. Abs.*, 1931, 25, 1046.

<sup>22</sup> E. E. Halls, *British Plastics*, 1932, 4, 152, 176, 231, 269; *Brit. Chem. Abs. B*, 1933, 78. W. Phillips and H. T. Richardson, *British Plastics*, 1932, 3, 332, 447, 502.

<sup>23</sup> P. Grodzinski, *Kunststoffe*, 1933, 23, 63; *Chem. Abs.*, 1933, 27, 2317.

<sup>24</sup> British P. 253,870, 1929, to F. Raschig Chemische Fabrik; *Chem. Abs.*, 1933, 27, 436.

<sup>25</sup> K. W. Raschig, British P. 319,806, 1928; *Chem. Abs.*, 1930, 24, 2624.

<sup>26</sup> British P. 363,166, 1930, to Herold A.-G.; *Chem. Abs.*, 1933, 27, 1531.

## BINDERS

Binders used in hot-molding compositions divide themselves naturally into two groups, requiring different treatment during pressing and yielding products of distinct characteristics. The first of these groups, which is also the older in point of industrial application, embraces resinous materials that remain permanently fusible, and includes the natural resins of which shellac is the most important example. The members of the second group have the property of undergoing a polymerization, or other chemical reaction, under heat which renders them permanently infusible after treatment. These are typified by the phenol-aldehyde and urea-aldehyde resins. Naturally, these two groups are not definitely defined and clearly differentiated. Rather they tend gradually to merge into each other with the dividing line determined by the definition of the term infusible. Many materials whose temperature of flow or fusion is increased by heat treatment still remain sufficiently fusible to put them into the first class under one set of conditions while permitting them to be considered as infusible under another.

Molding procedure should be adapted to this peculiarity of the resinous binder, which must in turn be adapted to the service required of the finished product.

**Fusible Binders.** Binders of this type, which include the natural resins, shellac, copal and rosin, were the original bases of molding compositions and one can trace the primary motive which led to the development of synthetic resins in an effort to improve shellac molding materials. In such a history, there has been a gradual development in the technique of handling fusible preparations to meet changing requirements. Shellac, for instance, is easily formed to produce articles of considerable toughness and a good surface finish, and has been extensively used for purposes where its relatively low softening point was not detrimental. The applications were many and as demand grew, particularly in the manufacture of phonograph records, the price of shellac naturally rose and encouraged the use of cheaper materials to extend or replace it.<sup>27</sup> Various natural resins, treated rosin and asphaltic compounds, as well as mixtures of these, came into prominence to take the place of the more expensive shellac, and finally a number of synthetic resins, cumarone, phenol-sulphur chloride and others of the fusible type have invaded this field. Cumarone resin, to which linseed oil has been added to overcome brittleness, and, more recently, vinylite resins have found some application in sound records. However, natural resins and mixtures of these with asphaltic compounds continue to dominate the field, despite threats from fusible synthetic types. It is doubtful if this condition could long continue should a fusible synthetic resin possessing the hardness and toughness of shellac, but with a higher softening point, be made cheaply available.

**Reactive Binders.** Reactive, thermosetting synthetic resins include the phenol-aldehyde and the urea-aldehyde reaction products as the most widely employed binders for molding compositions. Other resins are principally used for special purposes or to obtain certain desired properties. The resin binder for hot molding should have a relatively sharp melting point and be fairly liquid at the operating temperature to enable it to cover the fibrous filler properly and yield a sharp impression. Its fluidity, however, should not be so extreme as to permit it to separate from the filler and exude from the mold when pressed. It should be mobile enough to fill the cavity completely without requiring excessive pressure and at the same time sufficiently viscous to remain uniformly mixed with the filler.

<sup>27</sup> See description of phonograph record manufacture, in Chapter 68.

Resinous binders that soften but do not flow may be employed with an added flux or plasticizer. Resins quickly rendered infusible by heat are especially desirable from a production standpoint, but frequently require the addition of a flux to increase flow and permit their use in intricately shaped molds. Rapid hardening or fast cure allows molded articles to be made quickly by hot-pressing, often without the necessity of cooling the mold to avoid adhesion of the piece during ejection.

The time required for heat-treating must be fixed in proper relation to the type of composition employed and the shape and size of the piece to be made if uniformity of product is to be secured. Articles having thick walls or cross sections require a longer heating than thin-walled pieces, to allow the interior of the mass to be hardened properly. Undercured pieces may cause trouble in molding and never give the maximum of service.

The odor of a molding composition is usually that of the binder and, while normally this is not an important consideration, it cannot be entirely overlooked. The heat of molding temporarily accentuates this, but after cooling, the odor should not be so pronounced as to be objectionable under ordinary conditions. At the higher temperatures, the binder must neither liberate appreciable amounts of gas (creating an internal pressure in the mold and resulting in blistering of the finished piece) nor undergo decomposition (thereby effecting staining of or sticking to the mold).

Weaknesses in binders can often be partially offset by the proper choice of fillers or the addition of other substances to the composition. The mixing of binders that have different properties is frequently advantageous. No composition is ideal in every respect and the investigator in this field will find many opportunities for research.

#### FILLERS

Upon the proper selection and use of the filler, no less than of the binder, depend the qualities of finished molded products. When properly selected and blended with the binder, fillers are essential constituents of the molding composition, contributing largely to the mechanical strength and other valuable properties of the articles made from it. The choice of an appropriate filler must be based upon several factors affecting the final composition. Resins alone, when pressed or cast and cooled, develop internal strains and stresses resulting from contraction on cooling, which may lead to cracking. The effect of shrinkage can only be prevented by lengthy tempering or annealing of the piece through long heating and slow cooling. When fillers are added before molding, they perform the important function of minimizing this shrinkage and of offsetting its effect on the article. Fibrous materials are particularly useful in this way and in addition they improve the shock resistance and mechanical strength of the final product. While it is true that the cost of fillers on a volume basis is generally less than that of the resinous binder which holds them together, fillers should in no wise be considered adulterants, for choice based on this view is sure to reduce the value of the product. Many valuable properties of molded articles, in addition to strength and shrinkage, depend on the selection of a filler and a binder adapted to each other and to the problem in hand.

**Wood Flour.** Perhaps the most universally used filler in molding compositions of the thermosetting type is finely pulverized wood commercially known as wood flour. Although commonly termed a filler, it is likewise a reinforcing ingredient as it improves the shock resistance, yielding a tougher product whereas



the resin alone would tend to be fragile. It also contributes to the flowing properties of the composition. Wood flour is made from various species of trees, spruce, fir and white pine being used both in this country and Europe because they yield the better grades of flour of light color. A relatively high content of natural gum, as in long-leaf yellow pine, is undesirable, since compositions containing it require special treatment to counteract the effect of the natural resin. The characteristics of wood flour<sup>29</sup> to be considered are particle size and shape, bulk, natural gum content and color. Upon examination under a microscope the particles of the stock should show a fibrous structure and be fairly uniform in size. The material should be free from foreign substances, particularly those of a metallic or abrasive nature which might affect the dielectric properties of the product or injure the mold. Customarily about eighty per cent should pass through an 80 mesh screen. The moisture content, an important factor in dielectric strength, is determined<sup>30</sup> by loss in weight on heating at 105°C. for 24 hours and should not be over 5 or 6 per cent. The impregnation and mixing of wood flour with a resinous binder has a tendency to seal in any moisture that may be present in the filler, and, to obtain maximum insulating properties, the former should be thoroughly dried prior to use. When dry it is quite hygroscopic and, if not used immediately, should be stored in a tightly covered container or in a heated storage oven to prevent absorption of moisture from the air. The finished composition should be treated in the same manner. Color of the wood flour is not always important, but must be considered if light shades are desired. Shavings have been suggested<sup>30</sup> as a substitute for wood flour in certain cases.

**Asbestos.** Among the many grades of asbestos,<sup>31</sup> powder-like material, known as "floats" or micro-asbestos, is used extensively in compositions that are required to withstand, without carbonization, higher temperatures than could be resisted by wood flour or other organic fillers. Articles of good appearance can be molded from compositions containing a short-fiber asbestos, but these are mechanically weaker than those produced with the longer grades.

Care must be used in the mixing of preparations containing long-fiber asbestos to avoid undue breakage of the filler. This is best accomplished when the fibers are treated with the binder by the wet process subsequently described or are well mixed with a finely powdered resin, to which has previously been added the other ingredients. The blending should be done with a minimum of grinding action so that each individual fiber becomes coated with the binder. Since asbestos is a dense solid material, only a very slight amount of impregnation occurs in contrast with wood flour. A sufficient quantity of resinous binder should be employed to insure uniform coverage of each individual filament, as uncoated fibers will stick to the mold and cause blemishes in the surface of the piece. The longer-fiber compositions do not flow readily, requiring extreme care to secure a properly filled mold, and, in general, yield a product somewhat low in tensile strength but with good shock resistance. The surface is inferior to that obtained with wood flour and short-fiber asbestos.

Molded products containing asbestos usually have lower dielectric strength than those with organic fillers, since mineral fillers often include small amounts of metallic iron. A large proportion of the conducting component is in the dust and can be removed by screening through a 20-mesh sieve and discarding the fine material.<sup>32</sup>

<sup>29</sup> R. Meldau, *Z. Ver. deut. Ing.*, 1929, 73, 1315; *Chem. Abs.*, 1930, 24, 2246.

<sup>30</sup> Methods of test are described in Chapter 69.

<sup>31</sup> Swiss P. 128,831, 1927, to Emil Haefely & Cie A.-G.; *Chem. Abs.*, 1929, 23, 2772.

<sup>32</sup> H. Rosenberg, *Kunststoffe*, 1927, 17, 55; *Chem. Abs.*, 1927, 21, 1692.

<sup>33</sup> L. E. Barringer, *Gen. Elec. Rev.*, 1927, 30, 387.

Asbestos in the form of fabric treated with resinous binder is used to make laminated products capable of resisting high temperatures.

**Cotton Flock and Cotton Linters.** Cotton may be obtained in fibers of varying length and is usually employed in minor proportions as a filler for molding compositions of low heat resistance. It is commonly used in conjunction with powdered mica or gypsum, as it greatly increases the impact strength. Cotton flock has a tendency to cluster into small lumps when baled for shipment and should therefore be passed through a screen to break up these masses. Care is required in handling to prevent clotting and insure even distribution in the blended composition.

As cotton is also hygroscopic, the flock should be dried and stored in the same manner as wood flour, particularly if the composition is to be used for electrical insulation.

**Silk Flock.** Silk flock, like cotton flock, is used to increase the shock resistance. It replaces the latter principally in articles that are molded oversize and shaped by machining, since the inclusion of cotton results in a surface that polishes poorly. Silk flock has been found to be superior in this respect.

**Paper and Fabric.** In the manufacture of laminated products, paper and fabric are the important fillers, but paper is also used to some extent in other molding compositions, usually in the form of pulp or ground to a fibrous mass to replace wood flour. Fabric, impregnated with a binder, may be employed in molded articles to give high shock resistance, as in the case of golf club heads. The composition is difficult to mold into complicated shapes because of the poor flowing characteristics, but this may be offset in a measure by impregnating paper or fabric with a synthetic resin, then beating, and mixing with additional powdered binder.<sup>55</sup>

**Mica.** This material is very much in demand for electrical insulation because of its very excellent properties, especially its high insulating and dielectric values and its low losses, even at high frequencies. Resinous binders have been used to build up small flakes or sheets into larger forms, and Frederick<sup>56</sup> has made plates of mica while McCarthy<sup>55</sup> has prepared sheets by showering mica flakes on a machine bed, supplying a liquid binder and compacting the whole by rolling.

Mica alone or in conjunction with other inorganic fillers, such as gypsum, may be used with shellac or phenol-sulphur chloride resins to make molding compositions which may often contain 70 to 90 per cent by weight of these fillers and yield molded pieces of correspondingly high density. The use of 70 per cent of mineral filler with a shellac binder forms a mechanically strong composition, but the phenolic resin binders do not wet or cover particles of mica fully and consequently the strength expected from molding a preparation of this type is not realized. Mica must be finely ground if it is to be incorporated with a phenolic resin and a fibrous filler should be added to increase the mechanical strength. The alkyd resins are well adapted for use as binders for mica.<sup>56</sup> Lloyd<sup>57</sup> has suggested a phenol-urea-aldehyde resin to bond mica, as he finds that wetting occurs more easily. Furthermore, the product is claimed to give less trouble from "tracking" or breaking down and becoming conductive under the influence of an electric arc. Crossley<sup>58</sup> has combined mica with lead borate to form a synthetic

<sup>55</sup> R. Schroeder, M. Schroeder, S. Lewis and E. Jaroslaw, British P. 278,038, 1926; *Chem. Abs.*, 1928, 22, 2673.

<sup>56</sup> L. T. Frederick, U. S. P. 1,702,896, Feb. 19, 1929, to Chicago Mica Co.

<sup>57</sup> L. McCarthy, U. S. P. 1,622,795 and 1,622,796, March 29, 1927; *Chem. Abs.*, 1927, 21, 1693.

<sup>58</sup> L. E. Barringer, *Gen. Elec. Rev.*, 1926, 29, 757. See Chapter 49.

<sup>59</sup> A. Lloyd, U. S. P. 1,784,737, Dec. 9, 1930, to Bakelite, Ltd.

<sup>60</sup> P. B. Crossley, U. S. P. Reissue 15,727, Dec. 4, 1923; original 1,394,973, Oct. 25, 1921; *Chem. Abs.*, 1922, 16, 453. See also L. E. Barringer, *Gen. Elec. Rev.*, 1931, 34, 406. *Plastics*, 1931, 7, 495.

molding composition. A review of processes and materials employing mica has been given by Rossman.<sup>30</sup>

**Powdered Fillers.** Fine inorganic materials such as china clay, gypsum, rotten stone, barium sulphate, slate powder,<sup>40</sup> kieselguhr, siliceous and flint, are used to some extent in molding compositions, but they generally require a reinforcing fibrous or lamellar filler. Large quantities of powdered fillers can be used in certain cases, particularly when price is a factor. The proportion of mineral fillers is especially high in phonograph records, since great strength is not essential and hardness is required. Thermoreactive preparations are usually specified for products requiring greater strength and, therefore, should be incorporated with only a small quantity of mineral powders.

For uniform results the properties of fillers must not change appreciably from one shipment to another. Tests which serve to indicate these variations are also useful guides in the initial choice of a suitable material to meet specific requirements.<sup>41</sup>

Whyte and Lord<sup>42</sup> have incorporated up to 30 per cent of diatomaceous earth, of particle size less than 0.01 mm.<sup>43</sup> into synthetic resin or cellulose ester or ether films. They have reported increased resistance to abrasion and cutting without serious reduction in the transparency.

**Miscellaneous Fillers.** Carbon obtained by the thermal decomposition of graphitic oxides is sometimes of service in the manufacture of plastic materials,<sup>44</sup> as finely pulverized electrical conductors are used in molding compositions to lower the resistivity.<sup>45</sup> Ground ebonite has been suggested as a filler in molding preparations,<sup>46</sup> and Holt<sup>47</sup> has made articles from granulated cork mixed with a binder, while Messer<sup>48</sup> has used resin-coated cork to form articles reinforced with a metal core.

Rubber which has been vulcanized and ground may be employed as a filler, alone or with wood flour, according to Crosley.<sup>49</sup> Pierson<sup>50</sup> has made use of leather scrap in the preparation of a thermoplastic molding composition. Walton<sup>51</sup> has introduced relatively large pieces of furnace slag that have previously been colored by a vitreous coating. The resin is clear, and the filler serves mainly for decoration.

Abrasives have been incorporated in synthetic resin binders, but, in this case, voids should be left between the particles to give the clearances required for cutting. Cellulose acetate<sup>52</sup> and phenol-formaldehyde condensation products<sup>53</sup> have been suggested for this type of work. The abrasive may be coated with a

<sup>30</sup> J. Rossman, *Plastics*, 1928, 4, 549.

<sup>40</sup> J. F. Sacher, *Gummi-Ztg.*, 1933, 47, 439; *Brit. Chem. Abs.* B, 1933, 289.

<sup>41</sup> K. Ripper, *Plastics*, 1930, 6, 452. The most important tests are for fineness, oil absorption (Gardner-Coleman method), true and apparent density, moisture, color and in certain cases the chemical composition. For fineness or particle size see especially W. M. Weigel, *Tech. Paper, Bureau of Mines*, 1924, 296; *Chem. Abs.*, 1924, 18, 3687. See also, *ibid.*, 1925, 343; *Chem. Abs.*, 1926, 20, 665.

<sup>42</sup> S. Whyte and W. E. Lord, British P. 384,694, 1931, to Gramophone Co., Ltd.; *Brit. Chem. Abs.* B, 1933, 155.

<sup>43</sup> This is about one-quarter of the maximum diameter of a particle which will pass a 325 mesh screen.

<sup>44</sup> French P. 737,005, 1932, to Alexander Wacker Ges. für electrochem. Ind. G.m.b.H.; *Chem. Abs.*, 1933, 27, 1464.

<sup>45</sup> J. Bradley, British P. 273,025, 1926, to Metropolitan-Vickers Electrical Co.; *Brit. Chem. Abs.* B, 1927, 727.

<sup>46</sup> E. L. C. Liotard, French P. 701,411, 1930; *Chem. Abs.*, 1931, 25, 4096.

<sup>47</sup> A. Holt, British P. 358,592, 1930; *Chem. Abs.*, 1933, 27, 332.

<sup>48</sup> R. Messer, British P. 193,013, 1923, to Suberit-Fabrik (Nachfolger); *Chem. Abs.*, 1923, 17, 3580.

<sup>49</sup> F. J. Crosley, British P. 355,341, 1930, to India Rubber, Gutta Percha & Telegraph Works Co., Ltd.; *Chem. Abs.*, 1933, 27, 436.

<sup>50</sup> W. C. Pierson, U. S. P. 1,846,356, Feb. 23, 1933, to Leagum Corp. of Delaware; *Chem. Abs.*, 1932, 26, 2561.

<sup>51</sup> S. F. Walton, U. S. P. 1,781,204, Nov. 11, 1930, to Exolon Co.; *Chem. Abs.*, 1931, 25, 177.

<sup>52</sup> British P. 359,324, 1930, to Celluloid Corp.; *Chem. Abs.*, 1933, 27, 392.

<sup>53</sup> L. H. Baekeland, U. S. P. 942,803, Dec. 7, 1909; *Chem. Abs.*, 1910, 4, 680.

liquid resinous composition so as to form a non-tacky layer.<sup>54</sup> On the other hand, Brock<sup>55</sup> and Martin<sup>56</sup> have used mixtures which are more or less sticky and gummy, and Novotny<sup>57</sup> coated granules with an adhesive resin which is rendered non-tacky by freezing so that the loose mass may be levelled in the mold to form a uniform, well-balanced grinding wheel.

### COLORING AGENTS

Both dyes and pigments are employed for coloring molding compositions, dyes being preferred in products intended for electrical insulation. When the molded article is to be used with a material which may attack certain dyes, care must be exercised in the selection of the coloring agent. If high heat resistance is required, aniline dyes are sometimes employed, but pigments are more satisfactory over a long period of time. Bone black or carbon black, alone or mixed with a black aniline dye, is sometimes used, while iron oxide and the sienna and umber pigments may be blended in various proportions to obtain the red and brown shades. Manganese dioxide or pyrolusite gives a dark brown or black color.

The dye or pigment must always be very finely ground and thoroughly intermingled with the other ingredients of the composition to obtain an even, uniform shade and full color value. It should also be free from metallic content, to avoid any reduction in the dielectric strength of the molded product.<sup>57a</sup>

### LUBRICANTS AND PLASTICIZERS

The tendency of molding compositions to stick to the mold may be best overcome by the inclusion of a lubricant. Manufacturers of molding compositions guard against sticking by lubricating their materials properly for standard molding conditions, and little trouble should be encountered unless the shapes are very intricate. Stearic acid, stearates and metallic soaps are extensively used for such purposes.<sup>58</sup> The various resins used as binders in hot molding differ so in properties that no general rule can be made and the proper kind and amount of lubricant to be used with any particular composition can only be determined by actual test.<sup>59</sup>

Plasticity and the influence of plasticizers have been given considerable study by various investigators.<sup>60</sup> The primary purpose of including a plasticizer in a molding composition is to increase the flow of the material, thus insuring complete filling of the mold cavity and perfect reproduction, particularly with pieces of complex form. Insufficient flow may result from using too little binder, or it may be caused by too quick reaction of a thermosetting binder under the heat of the mold with consequent hardening of the composition before the press is closed. The difficulty can be overcome by cooling before charging but this increases molding time. Such a resin may have been taken to an unduly advanced stage of reaction before molding, a situation which would accelerate its hardening and prevent it from flowing freely. These conditions can all be improved by

<sup>54</sup> British P. 359,996, (1930), to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 435.

<sup>55</sup> F. P. Brock, U. S. P. 1,537,454, June 12, 1925; *Chem. Abs.*, 1925, 19, 2116.

<sup>56</sup> R. Martin, U. S. P. 1,626,246, Apr. 26, 1927.

<sup>57</sup> E. E. Novotny, U. S. P. 1,901,324, March 14, 1933, to J. S. Stokes; *Chem. Abs.*, 1933, 27, 3053.

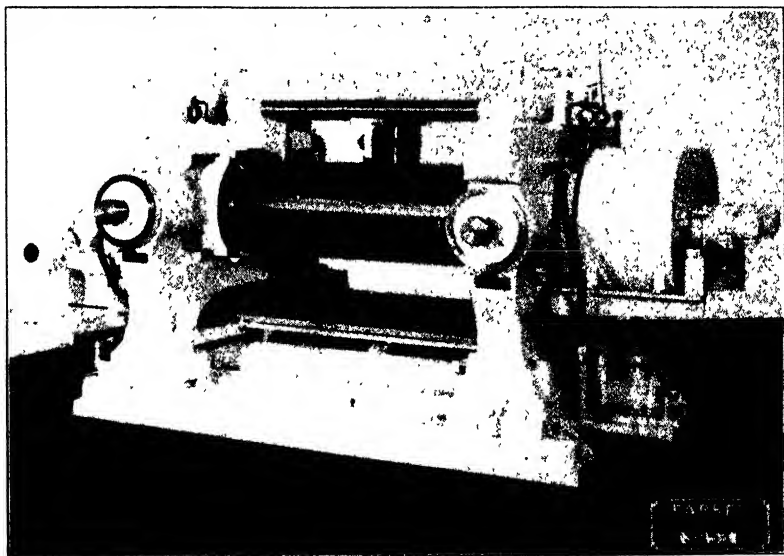
<sup>57a</sup> One method of incorporating dyes into molding compositions is to color the filler with the dye and then mix the filler with the resin. H. Clayton and H. Jones, British P. 419,446, 1934; *Chem. Abs.*, 1935, 29, 2628.

<sup>58</sup> Refer to Chapter 37 for a discussion of metallic soaps.

<sup>59</sup> Suggested methods for the treatment of sticking and staining are described in Chapter 68.

<sup>60</sup> O. Ruß, *Z. anorg. allgem. Chem.*, 1924, 133, 187; *Chem. Abs.*, 1924, 18, 1596. A. deWaele, *Kolloid-Z.*, 1925, 38, 27; *Chem. Abs.*, 1926, 20, 3605. O. Manfred and J. Obrist, *Kolloid-Z.*, 1927, 41, 248; *Brit. Chem. Abs. A*, 1927, 514; *ibid.*, 1927, 41, 174; *Chem. Abs.*, 1927, 21, 2991. M. Forrer, *Rev. gen. mat. plastiques*, 1932, 8, 259; *Chem. Abs.*, 1932, 26, 4521.

the addition of a plasticizer. This should be a solvent for the resin and in reactive compositions it should either undergo reaction and become infusible or remain in solid solution in the molded material. An excess of plasticizer or a substance incompatible with the composition will result in a spotted surface. Plasticizers may be added to the resin, to the filler or to the molding composition. To avoid surface blemishes or sticking and staining of the mold, it is essential that the mixing be thorough, an operation which may present difficulties.



*Courtesy Farrel-Birmingham Co., Inc.*

FIG. 169.—22" x 60" Heavy Duty Plastics Mill with Individual Drive.

In sheeted compositions, plasticizers are incorporated to lower the temperature at which the preparation may be worked, a consideration which is of importance if the material is to be packed in the mold prior to pressing.<sup>61</sup>

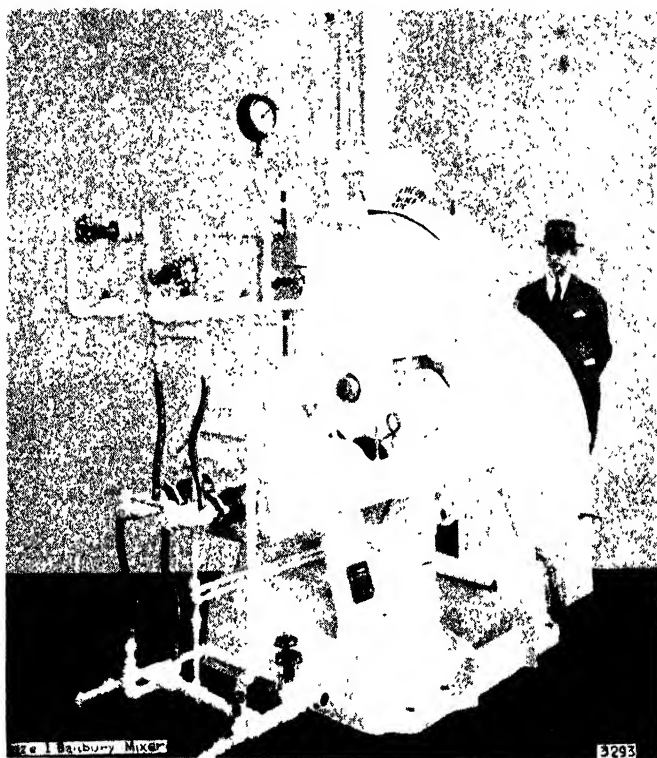
#### METHODS OF MIXING

The most widely used procedure for mixing the thermoplastic, and particularly the thermosetting, molding compositions is the "dry method" which eliminates the need for solvents and their subsequent removal and recovery. The process is largely restricted to preparations that are solid and sufficiently hard at normal temperatures to permit grinding without caking or sintering. Liquids may be added but they must be of such character and quantity that they will be distributed uniformly throughout the mix without wetting it to a plastic condition. When large amounts of liquids or soft plastic binders of low melting point are used, the wet process gives a more uniform product.

The dry method consists essentially of pulverizing the resinous binder and

<sup>61</sup> The various plasticizing agents and fluxes employed in molding compositions are discussed more fully in the chapters of this book devoted to the different types of resins. See particularly Chapter 22 dealing with phenol-aldehyde types and Chapter 28 for urea-formaldehyde resins.

grinding this with the other ingredients, lubricant, flux, hardening agent and dyes. The work may be done in a hammer mill or in a ball mill. The fibrous fillers such as wood flour, cotton flock or asbestos are then added and the blending continued until a uniform mixture is obtained. This must be done with a minimum of grinding action to preserve the length of the fibers, and it is sometimes advisable to mix a lubricant with the fillers as a separate operation before adding to the binder.



*Courtesy Farrel-Birmingham Co., Inc.*

FIG. 170.—Size 1 Banbury Plastics Mixer for Laboratory and Small Production.

The light, fluffy powder, prepared in this manner, may be given additional treatment by passing between heated steel cylinders revolving towards each other at slightly different speeds. These are so arranged that the distance between the rolls may be varied during operation at the will of the operator to process the material properly and obtain a sheet of the desired thickness. The advantages derived by further manipulation on heated rolls of this type are three-fold. A more intimate mixture of the ingredients is secured by fluxing the resinous binder and coating all of the particles. Second, there is closer adherence of the particles and a decided reduction in bulk or increase in the apparent density. The volume of the composition is an important factor, as sufficiently large mold cavities must be provided to contain the full charge necessary to form the article. With a very bulky material this may be too great for efficient molding and will tend to lower production. Minimizing the bulk also makes shipping more convenient.



of steam or other heating mediums. See Figs. 170 and 171. Use of masticators<sup>43</sup> obviates the need for fine grinding and blending of the ingredients in a ball mill as mastication is performed while the material is hot and plastic. Proper temperature control with thermosetting resins is essential and the hot mixture when removed from the masticator is usually cooled for a short period and then sheeted on differential rolls to chill it rapidly. Quick cooling is necessary as the mass will retain heat over a considerable period of time and may, in the case of thermosetting binders, be converted to the infusible stage.

**Uniformity of Mixture.** The methods thus far described generally require an elevated temperature to effect mixing. When the thermosetting compositions are prepared in this manner, care must be exercised to prevent the reaction from proceeding to an extent that would reduce the plasticity of the mixture and make it difficult to mold properly. Skilled operators are therefore needed and every facility must be afforded for the proper regulation of the mixing process to insure uniform molding characteristics. Control of the progress of the reaction is a somewhat difficult matter at best, and blending of various batches of soft and hard material may be necessary to keep the product within the desired limits of plasticity.

**The Varnish Method.** The varnish method of mixing is of value when heat is to be avoided, since mobility of the ingredients is attained by dissolving the binder in a volatile vehicle, yielding a solution to which the filler and other insoluble components may be added. The material is usually worked in a masticator, which may, however, be of much lighter construction than that previously described because of the lowered viscosity. Mixing is effected by blades which rotate at different speeds and may be periodically reversed. These machines may be equipped with a steam jacket but heat is seldom used. A solution containing approximately 50 per cent of resin and having a relatively low viscosity is thoroughly absorbed by a wood flour filler at normal temperature and the danger of the reaction proceeding too far prior to molding is greatly decreased by this method.

The blended composition is then freed from solvent by drying. Non-reactive, fusible compositions may be satisfactorily treated in ordinary atmospheric dryers but the reactive thermosetting preparations, because of their sensitivity to heat, often require the lower temperatures of vacuum drying. Either shelf or rotary drum dryers can be employed.<sup>44</sup> Following the extraction of solvents, the product is ordinarily ground to a powder and is then ready for use. When sheet stock is desired the granulated material may be placed on rolls of the type already described for mixing, heated to a temperature sufficient to render it plastic and immediately passed through sheeting rolls.

### LAMINATED PRODUCTS

The raw material for making laminated products consists of sheets of paper or fabric impregnated with a resin solution and subsequently dried. By combining a number of such sheets and subjecting them to heat under heavy pressure to bind them firmly together, sheets, tubes,<sup>45</sup> rods and other simple shapes of any desired thickness may be made. These laminated products have exceptionally high tensile and impact strength combined with the other properties found in molded

<sup>43</sup> One type of masticator, known as the Banbury mixer (*cf.* Figs. 167, 171 and 172), provides facilities for the quick handling of raw ingredients, close temperature control and rapid production of mixed material.

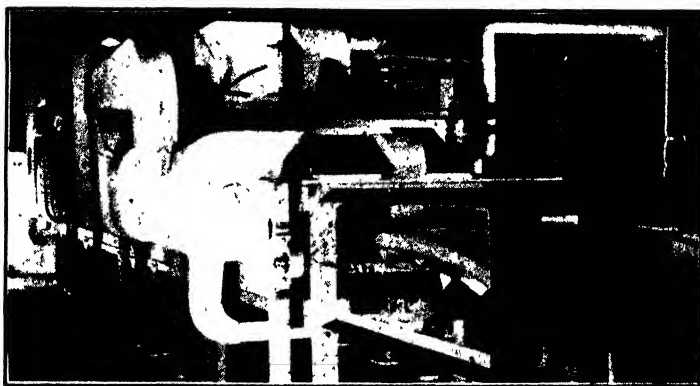
<sup>44</sup> The manufacture of phenol-aldehyde resin molding compositions is described in Chapter 22.

<sup>45</sup> W. C. Anderson, U. S. P. 1,595,811, Aug. 10, 1926, to Continental Fiber Co.; *Chem. Abs.*, 1926, 20, 3250.



articles<sup>66</sup> but cannot be molded into intricate designs without special preparation and shaping since the material itself has very little flow.<sup>67</sup>

**Preparation of Laminated Products.** Continuous sheets of paper, fiber or fabric are impregnated with a solution of resinous binder (usually containing 50 per cent total solids) and subsequently dried. See Fig. 172. The operation can be carried out in a manner similar to that used for coating paper, by passing the sheet between rolls, one of which is coated with the resin solution. The material, thus coated on one side, is passed over heated rolls to evaporate the solvent.<sup>68</sup> An alternate treatment is to cover one surface of the fabric or paper with a binder of dough-like consistency, using scrapers similar to those on a rubber spreading machine. If both sides of the sheet are to be coated, dipping in a solution of the binder is the simplest and most effective procedure. The excess may be removed by scrapers and the sheet is then led through a drying chamber maintained at a properly regulated temperature. The heat incident to the last



*Courtesy Modern Plastics*

FIG. 172.—Fabric-Impregnating Machine. Paper or fabric is treated with synthetic-resin solutions in this apparatus. After the treated material has been dried, layers of it are hot-pressed to form laminated products.

step effects a partial reaction of the resin which must not be allowed to go too far lest the finished pressed product be weakly bound together.

Sheets containing a resinous binder may be formed in a paper beater by dispersing pulp or other available fiber in liquid resins, or finely pulverized resins suspended in water, the product being later formed into a sheet on screens or in a paper making machine.<sup>69</sup> If the resin is thermosetting, a hardening agent can be added, but in this event the sheet is best dried in a vacuum or on calendering rolls heated to a low temperature,<sup>70</sup> so as to minimize further hardening of the binder. The progress of the reaction can be retarded by drying at a temperature below 40°C. while passing through a zone of reduced pressure,<sup>71</sup> or by treat-

<sup>66</sup> H. W. Rowell, *J.S.C.I.*, 1927, 46, 573, 592.

<sup>67</sup> The products and methods which are especially adapted to phenol-aldehyde laminated materials are described in Chapter 22, while the methods of testing are discussed in Chapter 69.

<sup>68</sup> D. J. O'Connor, Jr., U. S. P. 1,284,432, Nov. 12, 1918, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1919, 13, 170.

<sup>69</sup> L. H. Baekeland, U. S. P. 1,160,362 and 1,160,365, Nov. 16, 1915, to General Bakelite Co.; *Chem. Abs.*, 1916, 10, 256. C. A. Haanen, U. S. P. 1,630,434, May 31, 1927, to Felten & Guillaume Carlswerk A.-G.; *Chem. Abs.*, 1927, 21, 2335. J. Mursch, U. S. P. 1,869,491, Aug. 2, 1932, to Joseph Gatti; *Chem. Abs.*, 1932, 26, 6440. See also J. d'A. Clark and H. A. Kidd, U. S. P. 1,996,951, Apr. 9, 1935, to Mead Research Engineering Co.

<sup>70</sup> L. V. Redman and H. C. Cheetham, U. S. P. 1,551,423, Aug. 25, 1925, to Bakelite Corp.; *Chem. Abs.*, 1926, 20, 267. J. Rossmann, *Paper Trade J.*, 1929, 89 (2), 61; *Chem. Abs.*, 1929, 23, 5589.

<sup>71</sup> G. E. Wightman, U. S. P. 1,703,414, Feb. 26, 1929, to Bakelite Corp.; *Chem. Abs.*, 1929, 23, 2002.

ment with a current of warm dehydrating gas at a temperature below that at which excessive softening of the reactive resinous binder occurs.<sup>73</sup> The use of wood flour has been advocated to aid in the more uniform incorporation of pulverized resinous binders and fluxing agents in paper pulp<sup>74</sup> which is to be sheeted in a paper making machine. Powdered mica in the form of a thick paste, when added to the paper stock before mixing, is stated to give high electrical resistance.<sup>74</sup>

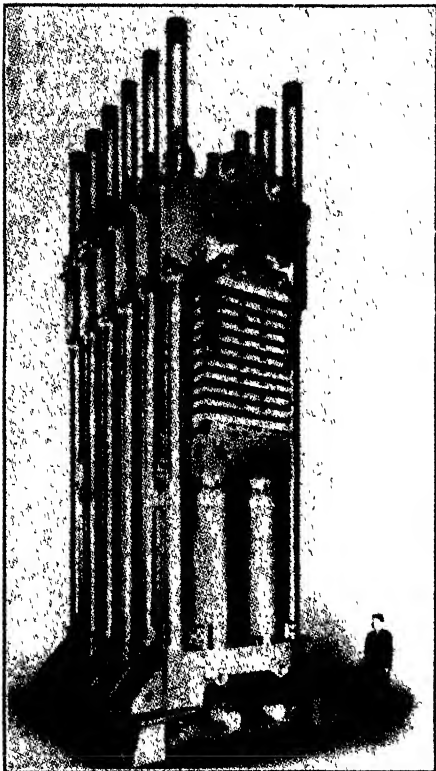


FIG. 173.  
Multiple-Platen Press for Curing Finished Sheets.

*Courtesy R. D. Wood Co.*

In the manufacture of laminated pressboard, it is important to adjust the proportion of resinous binder carefully, although standard material usually contains approximately 50 per cent by weight of reactive resin. Water resistance must be high, the usual specification for phenolic resins requiring that the absorption after total immersion for 24 hours must not exceed 0.2 per cent. If the resin content falls below 47 per cent, the water absorption may exceed this value, but if greater than 55 per cent the sheets are likely to slip over one another in the press.

Slow curing is desirable and frequently is conducted at a low enough tempera-

<sup>73</sup> L. H. Baekeland, U. S. P., 1,842,647, Jan. 26, 1932, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 1812. British P. 314,937, 1928; *Brit. Chem. Abs. B*, 1930, 111. French P. 663,551, 1928; *Chem. Abs.*, 1930, 24, 699.

<sup>74</sup> A. L. Clapp, U. S. P. 1,684,755, Sept. 18, 1928; *Chem. Abs.*, 1928, 22, 4757.

<sup>74</sup> G. J. Crossman, U. S. P. 1,868,560, July 16, 1932, to Panelyte Corp.; *Chem. Abs.*, 1932, 26, 5441. The impregnated sheets formed by these methods are cut into convenient lengths and hot pressed as described in Chapter 63, or marketed as unpressed sheets to be formed as desired by the purchaser.

ture to allow the treatment to continue for half an hour. Subsequent baking may be resorted to for additional hardness and water resistance.

In addition to the method of impregnating sheets of fabric by coating or dipping the previously woven material, other procedures have been suggested by which the individual threads or cords are treated and subsequently dried. The product may be then formed by placing a mass of the threads into a mold in a haphazard manner to form irregular or interlocking structures<sup>74</sup> or they may be woven into a fabric.<sup>75</sup> Laminated sheets and articles containing a reactive resinous binder may be so formed that the interior portion will not harden to the same degree as the surface. This effect is secured by impregnating the outer layers with a binder containing a greater proportion of the hardening ingredient.<sup>76</sup>

Wood veneer has been utilized as a basis for laminated products, but the thin sheets intended for this purpose may have to be prepared with an alkaline solution before processing in order to prevent sticking to the platen of the press.<sup>77</sup> When coated with a solution of phenol-formaldehyde resin the veneer is liable to warp, and therefore Loetscher<sup>78</sup> has advised placing a partially dried sheet of resin-impregnated paper between the uncoated surfaces of wood which are to be united. Heat and pressure are then applied to form a composite layer. Saturation of the wood under vacuum has been recommended for improving the product, particularly for electrical purposes.<sup>79</sup> Panels containing a middle layer of flexible fibrous material impregnated with a reactive resin to which the outer surfaces may be cemented by hot pressing,<sup>80</sup> and wood veneer combined with a backing or transparent facing sheet of paper treated with a resin,<sup>81</sup> have also been suggested.

Sheets of glass may be united by a plastic to form a shatterproof material, the usual form consisting of two layers of glass with an interposed film of celluloid or cellulose acetate, the whole bonded together to form a composite plate. Many types of synthetic resins have been suggested for use in laminated glass not only as a cementing agent but also as the inner layer.<sup>82</sup>

<sup>74a</sup> P. S. Smith, U. S. P. 1,557,730, Oct. 20, 1925, to Products Protection Corporation.

<sup>75</sup> A. L. Brown, U. S. P. 1,673,797, June 19, 1928, to Bakelite Corporation.

<sup>76</sup> A. L. Brown, U. S. P. 1,559,846, Nov. 3, 1925, to Bakelite Corporation.

<sup>77</sup> E. C. Loetscher, U. S. P. 1,876,329, Sept. 6, 1932.

<sup>78</sup> E. C. Loetscher, U. S. P. 1,891,430, Dec. 20, 1932.

<sup>79</sup> J. R. Brossman, U. S. P. 1,834,895, Dec. 1, 1931, to General Electric Co.; *Chem. Abs.*, 1932, 26, 1092.

<sup>80</sup> R. W. Seabury, U. S. P. 1,625,749, April 19, 1927; to Radio Frequency Laboratories, Inc.; *Chem. Abs.*, 1927, 21, 2054.

<sup>81</sup> E. E. Novotny and C. J. Romieux, U. S. P. 1,597,538, and 1,597,539, Aug. 24, 1926, to John S. Stokes; *Chem. Abs.*, 1926, 20, 3355.

<sup>82</sup> This use of synthetic resins is treated in the various sections which describe specific preparations. Particular reference should be made to Chapters 22, 30, 34 and 52.

## Chapter 66

### Cold Molding

The process generally known as cold molding was introduced into the United States in 1909. The name was given to distinguish it from the molding of permanently thermoplastic compositions such as shellac, which of course require both heating and cooling. The phenolic heat-hardening plastics were not developed until slightly later.<sup>1</sup>

In general, cold-molding compositions, in the form of loose, slightly sticky powders, are subjected to high pressures in a very short cycle so that the press costs are low. The binders generally employed are cheap asphalts or pitches, which are hardened in the rather slow but inexpensive subsequent baking operation, mainly by evaporation of the solvent. Cold-molded objects can thus be made cheaply even though a two-stage process is used.

The cold-molding industry developed very rapidly and at one time nearly dominated the field of heat-resistant molded products in the United States. Cheaper heat-reactive compositions and the extensive use of multiple-cavity molds and automatic presses, however, have brought the hot-molding type of material into increasing favor because of the greater resistance to shock, lighter weight and better surface finish that are obtainable.<sup>2</sup>

The cheapness of cold-molding is its principal advantage and consequently the binders must be available at low cost. Although some synthetic resins have been employed, these have generally proved too expensive to compete with cheaper materials and mixtures. Even shellac, which has been included at times to a considerable extent in articles of this kind, is displaced by less expensive resins, pitches and asphalts. Thus, because cold molding does not appear to offer a wide field of usefulness for synthetic resins, it is discussed in less detail than hot-molding operations (see Chap. 65). Its interest is mainly as a competitive technique rather than one extensively applied to synthetic resins.

**Uses of Cold-Molded Articles.** One of the principal uses for cold-molded products is in the field of electrical insulation.<sup>3</sup> Other applications also take advantage of the high resistance to heat resulting from the baking treatment to which the molded pieces are subjected, a property entirely lacking in articles made with permanently fusible resinous binders. Cold-molded articles may possess even greater heat-resistance than most hot-molded products.

The exactness of dimension, mechanical perfection and lustrous surface finish obtained by hot molding can in no wise be secured in cold-molded articles. (See Fig. 174.) However, since, inserts may be incorporated with the latter (as with hot-molded articles) they may be used in enclosed equipment where appearance

<sup>1</sup> A. J. Weith and A. V. H. Morv, "Twenty-Five Years of Chemical Engineering"; D. Van Nostrand & Co., New York, 1933, 215.

<sup>2</sup> For a comprehensive comparison of the various methods of molding see Chapter 68. E. Hemming has given a great deal of information especially on cold-molding compositions in his book, "Plastics and Molded Electrical Insulation," Chemical Catalog Co., New York, 1923.

<sup>3</sup> H. Chase, *Electrical Mfg.*, 1933, 11 (2), 13; *Chem. Abs.*, 1933, 27, 2536.

is of no consequence and dimensional requirements are not exacting, particularly when resistance to heat and low cost are considerations of importance.<sup>4</sup>

**Binders and Their Solvents.** The usual binder employed in cold-molding operations is a pitch or an asphalt. Coal-tar pitch admixed with gilsonite is a useful binding composition. The better grades of cold-molding compositions frequently contain varying proportions of drying oils. The addition of stearin pitch is also considered beneficial. The mixture is dissolved in a composite solvent which is made up of a light volatile solvent such as benzol or V. M. & P. naphtha, and a heavy solvent of which anthracene oil is representative. The light volatile solvent serves to dissolve the pitch and gilsonite forming a solution having good penetrating powers, thereby easily mixing with the filler. The purpose of the heavy solvent is to maintain the material plastic on exposure so that it will not dry out completely when kept adjacent to the presses during molding. Enough

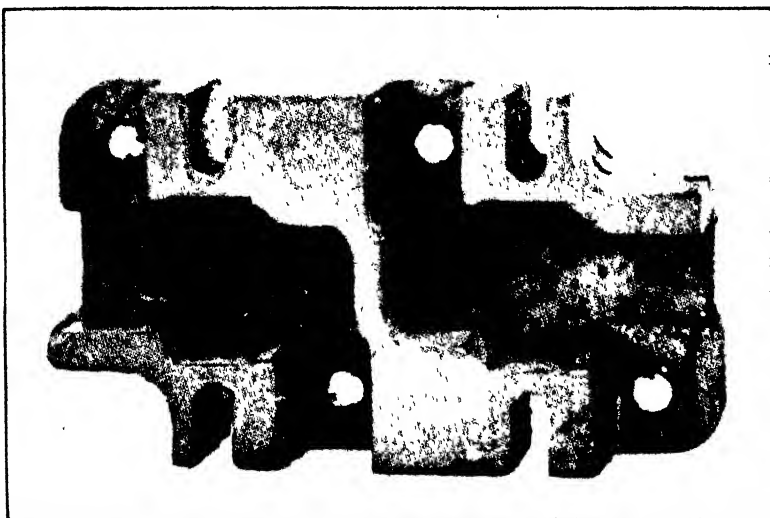


Fig. 174.—Cold-Molded Article.

solvent is present to render the composition plastic or slightly moist, permitting rapid molding. The material is partly dried to remove some solvent preparatory to pressing.

**Special Compositions.** The foregoing description indicates the general composition of cold-molding mixtures but modifications are numerous. Even vegetable albumin and casein may be mixed with various fillers to form compositions which can be cold-pressed.<sup>5</sup> Cold-molded articles are sometimes made from asphaltum (softened by the addition of benzol or gasoline) and hydraulic cement, or plaster of Paris, with water added. Objects molded from this composition, with an asbestos filler, are allowed to set and are finally baked or immersed in hot oil to eliminate moisture and fill the pores so as to increase resistance to water.<sup>6</sup>

The following serve as further illustrations of various compositions which are

<sup>4</sup> W. B. Stoddard, *Plastic Products*, 1932, 8, 191.

<sup>5</sup> F. G. Wiechman, U. S. P. 853,995, April 7, 1908; *Chem. Abs.*, 1908, 2, 2457.

<sup>6</sup> C. Batcheller (U. S. P. 1,995,412, Mar. 20, 1935) has prepared a cold-molding composition consisting of asbestos, calcined magnesite, powdered clay (Bentonite) and water.

a departure from the typical ones previously described. Cushing<sup>7</sup> made a mixture of asbestos or other filler with tung oil varnish, stearin pitch and coal-tar pitch being added to prevent the binder from oxidizing too rapidly. A granular mass is obtained which can be cold-molded and then baked for 24 hours at a gradually increasing temperature up to 205°C. A binder composed of tung oil, tar acids and sulphonates from tar acids treated with formaldehyde or hexamethylenetetramine has been suggested by Carter.<sup>8</sup> Steinberg<sup>9</sup> recommended a mix of asbestos, sulphur, coal-tar pitch, stearin pitch and castor oil containing benzol as the solvent, which could be molded without heat at 3-5 tons per square inch pressure and baked at a temperature increasing gradually to 232-250°C. over a period of 24 hours. This, it is stated, yields a tough, durable, insulating product which will resist temperatures approaching those employed in baking, without softening or deformation. Barringer has employed sulphurized oils as described in Chapter 60.

A composition applicable for cold-molded electrical fittings<sup>10</sup> comprises asbestos (40 parts), slate flour (40 parts), asphalt (8 parts), oxidized oil and a drier (8 parts), copal resin or similar material (2 parts). Chosa<sup>11</sup> advocated a process in which heat was employed to mix the ingredients. For example, 40 parts of stearin pitch and 60 parts of asphalt are heated to 245°C., 10 parts of castor oil are added and the temperature raised to 260°C. The mixture is then cooled to 93°C and thinned with 25 parts of benzol. When cold, 286 parts of this binder are incorporated with 1100 parts of asbestos, 66 parts of sulphur (as a "vulcanizing" agent) and 22 parts of iron oxide to form a composition which, particularly after storage, can be molded cold and cured by heating for a period varying from a few hours to more than 24 hours at a temperature rising gradually from 93°C. to 260°C.

Herbst<sup>12</sup> suggested the utilization of a binding agent, such as asphalt, with a polymerizing oil and a solvent together with a filler and an impregnating material, as for instance, furfural.

Articles of fairly high impact strength have been obtained with a composition described by Kurath and Richardson.<sup>13</sup> The binder consisted of stearin pitch, coal-tar pitch, gilsonite, fish or castor oil, and a solvent, together with a filler, a mixture of asbestos, sulphur and iron oxide. This material is formed into thin sheets which are shredded into flakes. The latter give laminations in the molded product and thus increase its resistance to shock.

Colored cold-molding compositions have been made by Coleman<sup>14</sup> from linseed oil, copal, and an asphalt by the addition of iron oxide ground with a dispersing agent and asbestos fiber. The fatty acids of drying oils may be employed as the dispersing material.<sup>15</sup> Bleecker<sup>16</sup> molded acid-proof objects from a pitch binder and a graphite or carbon filler which, after drying, were impregnated with a bituminous substance.

Shellac was molded by Daniels and Snell<sup>17</sup> to form an infusible, insoluble mass,

<sup>7</sup> W. T. Cushing, U. S. P. 1,255,139, Feb. 5, 1918; *Chem. Abs.*, 1918, 12, 983.

<sup>8</sup> W. W. Carter, U. S. P. 1,251,863, Jan. 1, 1918; *Chem. Abs.*, 1918, 12, 708.

<sup>9</sup> W. H. Steinberg, U. S. P. 1,233,415 and 1,233,416, July 17, 1917; *Chem. Abs.*, 1917, 11, 2566.

<sup>10</sup> F. J. Groten, Jr., U. S. P. 1,655,388, Jan. 3, 1928; *Chem. Abs.*, 1928, 22, 1019.

<sup>11</sup> C. F. Chosa, U. S. P. 1,671,229 and 1,671,230, May 29, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 2644.

<sup>12</sup> C. A. Herbst, U. S. P. 1,966,094, July 10, 1934, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1934, 28, 5612.

<sup>13</sup> F. Kurath and L. Richardson, U. S. P. 1,674,287, June 19, 1928, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1928, 22, 2819.

<sup>14</sup> E. E. Coleman, U. S. P. 1,825,620, Sept. 29, 1931, to Monowatt Elec. Corp.; *Brit. Chem. Abs. B.*, 1932, 614.

<sup>15</sup> E. E. Coleman, U. S. P. 1,799,004, March 31, 1931, to Monowatt Elec. Corp.; *Chem. Abs.*, 1931, 25, 3100.

<sup>16</sup> W. F. Bleecker, U. S. P. 1,587,750, June 8, 1926; *Chem. Abs.*, 1926, 20, 2567.

<sup>17</sup> E. A. Daniels and H. S. Snell, U. S. P. June 19, 1928, to Western Electric Co., covering the use of various hardening agents as follows: 1,673,803, triphenylguanidine; 1,673,804, aldehyde ammonia;

but the method of preparation is more like that used for cold-molded compositions. A filler (wood flour) is mixed with an alcohol solution of shellac to which a hardening agent, such as triphenylguanidine, has been added. The powder is dried at low temperatures and may be pressed at 260-270°F.

An inorganic binder, for example sodium silicate, mixed with cement and asbestos can be employed in the preparation of cold-molded objects. Such articles are utilized mainly for flame-proof insulation of extremely high heat-resistance, e.g., to insulate the heating element of an electric flat-iron from the upper portion and reflect the heat toward the bottom plate. Following the molding operation, articles made from this type of composition are usually baked at a high temperature, steamed in an autoclave, and then baked again.

**Synthetic Resin Binders.** Many synthetic resins have been proposed to replace part or all of the cheaper pitch compositions and some have had actual commercial use in spite of the higher cost.

Hemming<sup>18</sup> has investigated the utilization of phenol-formaldehyde condensation products. The binder was made from phenol and an excess of formaldehyde, with ammonia as a catalyst. This mixture was heated under reflux until its specific gravity reached approximately 1.17. It was then incorporated with asbestos or other filler to yield a granular or lumpy mix. The composition was molded cold under high pressure and, as soon as the article was shaped, it was placed in an oven and baked until hard. Grünwald<sup>19</sup> suggested mixing a plastic phenol resin and a filler, e.g., asbestos or sawdust, with non-solvents, such as a mixture of water and benzene, to obtain a flaky material, which could be molded cold, dried and then heated to cure the binder.

McCoy<sup>20</sup> also employed synthetic resins. One procedure involved dissolving a phenol resin, shellac or copal in a solution of a weak alkali (e.g., borax) mixing this with a filler, and precipitating the binder with tannic acid. A second method was to swell an infusible resin or pitch such as wurtzilite by adding a mixture of alcohol and benzol and then to incorporate a filler and a soluble binder.<sup>21</sup> He also suggested a mixture of phenol resin and cumarone resin.<sup>22</sup> Phenol-acetaldehyde<sup>23</sup> condensation products have been used as cold-molding binders. Such compositions do not set on heating but retain thermoplastic properties.

It has been suggested that friction materials which are to be subjected to molding may be saturated with an oxidizable binder, with apertures through the material to permit the escape of volatile substances.<sup>24</sup>

Cold-molding phenolic compositions have been prepared by Redman, Weith and Brock.<sup>25</sup> They recommend moistening wood flour or asbestos with a solution of hexamethylenetetramine in a phenol (particularly cresol), adding a potentially reactive resin in powdered form and pressing at room temperature. The molded article is later baked to transform the binder into an infusible and insoluble product. Another method is to mix 50 parts by weight of cresol with 13 parts of hexamethylenetetramine, incorporate this with 600 parts of asbestos pulp and 150 parts of long fiber asbestos in a kneading machine at room temperature and finally add 300 parts of fusible resin. The product is molded cold and

1,673,805, aminonaphthalene; 1,673,806, diphenylamine or other secondary aromatic amines; 1,673,807, reaction product of piperidine and carbon bisulphide; and 1,673,808, sodium  $\beta$ -naphtholate; *Chem. Abs.*, 1928, 22, 2850.

<sup>18</sup> E. Hemming, U. S. P. 1,125,906, Jan. 19, 1915; *Chem. Abs.*, 1915, 9, 731.

<sup>19</sup> F. Grünwald, U. S. P. 1,330,444, Feb. 10, 1920; *J.S.C.I.*, 1920, 39, 372A.

<sup>20</sup> J. P. A. McCoy, U. S. P. 1,237,466, May 22, 1917; *Chem. Abs.*, 1917, 11, 2173.

<sup>21</sup> J. P. A. McCoy, U. S. P. 1,384,370, Dec. 3, 1918; *Chem. Abs.*, 1919, 13, 367.

<sup>22</sup> J. P. A. McCoy, U. S. P. 1,425,784, Aug. 15, 1923; *Chem. Abs.*, 1923, 16, 3354.

<sup>23</sup> E. E. Novotny, U. S. P. 1,670,660, March 8, 1921; *Chem. Abs.*, 1921, 15, 1975.

<sup>24</sup> British P. 387,124, 1933, to Raybestos Co.; *Brit. Chem. Abs. B.*, 1933, 256.

<sup>25</sup> L. V. Redman, A. J. Weith and F. P. Brock, U. S. P. 1,339,184, May 4, 1920, to Redman Chemical Products Co.; *J.S.C.I.*, 1920, 39, 460A.

then baked for 2-20 hours at a gradually increasing temperature ranging up to 160° or 200°C. Although the ratio of binder to filler may be varied, the best proportion is 30 per cent of binder to obtain a flame-proof material. A modification<sup>26</sup> consists in mixing a fusible resin with hexamethylenetetramine at 66°C., proportioning the two to yield a product containing 1 methylene group for each phenol group. It is desirable to add to the binder about 5 per cent of its weight of a slowly volatile solvent such as creosote oil. The binder is mixed with 3 times its weight of asbestos and the product dried by exposure to warm air and ground to a coarse powder. This composition may be molded cold and baked for a prolonged period, starting at 38°C. and increasing the temperature gradually to approximately 230°C. Solutions which contain no hardening agent for the phenol-formaldehyde condensation product have also been reported as satisfactory binders. Ethylene glycol, hexalin, ethylene dichloride and Cello-solve were mentioned as applicable solvents.<sup>27</sup> Brock<sup>28</sup> used a powdered fusible phenol resin, with sufficient hardening agent and a plasticizer such as furfural, as a binder for carborundum.

Richardson also suggested the use of condensation products of a phenol and hexamethylenetetramine,<sup>29</sup> the proportions being 6 molecular equivalents of phenol to 1 of hexa. Reaction is continued until approximately one-third completed and then checked by the addition of 5 per cent of light coal-tar oil, after which a filler (asbestos) is added to give a composition containing 30 per cent of binder. This mixture is then dried at normal temperature and ground. A similar binder may be prepared with aqueous formaldehyde and an acid condensing agent such as hydrochloric acid.<sup>30</sup> Turkington has described a binder consisting of a potentially reactive phenol resin and furfural, which, when incorporated with a filler, may be molded cold. The articles so produced are heated to transform the reactive resin but not enough to vaporize the furfural, thus avoiding surface alterations or shrinkage.<sup>31</sup>

A binder for cold-molding compositions may be prepared by gradually adding paraldehyde to phenol or cresol and slightly acidulating with concentrated hydrochloric or sulphuric acid. The paraldehyde is converted to acetaldehyde, the conversion absorbing the heat evolved by interaction of the phenol and acetaldehyde. The reaction is first allowed to proceed in the cold, then the ingredients are heated to form a resin and the acid neutralized. The product, dissolved in acetone, is mixed with asbestos to form a molding composition. A hardening agent, such as hexamethylenetetramine, may be added. Wood flour may also be impregnated with such a solution, and a lubricant, for example aluminum palmitate, added when grinding the composition.<sup>32</sup> Commercial ortho-cresol heated with formaldehyde or paraform yields a resinous material, which forms a satisfactory binder when dissolved in acetone and mixed with a drying oil before incorporating with a filler. The resulting mass, dried in air and ground, can be molded in the cold and baked at a gradually rising temperature.<sup>33</sup>

Weber<sup>34</sup> suggested the use of a very reactive binder made from cresol and formaldehyde in the presence of a catalyst such as magnesium oxide. This is mixed

<sup>26</sup> L. V. Redman, A. J. Werth and F. P. Brock, U. S. P. 1,358,394, Nov. 9, 1920, to Redmanol Chemical Products Co.; *Chem. Abs.*, 1921, 15, 418.

<sup>27</sup> C. A. Nash and R. S. Daniels, U. S. P. 1,989,243, Jan. 29, 1935, to Bakelite Corp.; *Chem. Abs.*, 1935, 29, 1904.

<sup>28</sup> F. P. Brock, U. S. P. 1,537,454, May 12, 1925; *Chem. Abs.*, 1925, 19, 2116.

<sup>29</sup> L. T. Richardson, U. S. P. 1,842,067, June 1, 1920, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1920, 14, 2244.

<sup>30</sup> L. T. Richardson, U. S. P. 1,508,124, Sept. 9, 1924, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1924, 18, 3453.

<sup>31</sup> V. H. Turkington, U. S. P. 1,503,392, July 29, 1924; *Chem. Abs.*, 1924, 18, 2948.

<sup>32</sup> Carleton Ellis, U. S. P. 1,500,803, July 8, 1924; *Chem. Abs.*, 1924, 18, 2817.

<sup>33</sup> Carleton Ellis, U. S. P. 1,645,693, Oct. 13, 1927; *Chem. Abs.*, 1928, 22, 174.

<sup>34</sup> H. M. Weber, U. S. P. 1,536,253, May 5, 1925, to Ellis-Foster Co.; *Chem. Abs.*, 1925, 19, 1986.



with a filler and dried in a vacuum to minimize further reaction of the binder. The composition is then roughly shaped by cold molding, followed by hot pressing to complete the reaction of the binder and give the article its final shape. A somewhat similar binding agent was recommended by de Jarny,<sup>35</sup> who condensed phenol or cresol with aqueous formaldehyde in which 15 per cent or more of calcium chloride had been dissolved. The resin in the fusible stage is incorporated with a filler and the composition, when dried, can be pressed cold and heat-treated in the customary manner with or without a mold.

Prouty<sup>36</sup> employed phenol-formaldehyde resins as temporary binders for molded insulation composed of talc. The mixture is molded into the desired shape under pressure, which for spark plug cores may be 25,000 pounds per square inch. After heating the blank at 100-200°C. it can be machined to final shape and size and following this operation it is subjected to a temperature of about 1000°C.

Coleman and Groten<sup>37</sup> have prepared a cold-molding composition containing only a liquid drying oil and a varnish as a binder. This was heated to evaporate the solvent and oxidize the oils, after which a heat-convertible phenolic resin was added and the product molded. Cheetham<sup>38</sup> has described the utilization of a neutral aqueous suspension of a phenolic resin.

A binder comprising the reaction product of phenol or cresol and sulphur chloride is recommended by Votapek.<sup>39</sup> The product may be improved by adding a small quantity of stearin pitch, and incorporation of a filler, for example asbestos, is facilitated by the use of acetone or coal-tar oil as solvents. Trickey and Miner<sup>40</sup> suggested furfuryl alcohol, treated with sulphuric acid, as a binder. McCoy<sup>41</sup> has employed indene, cumarone or their isomers for this purpose. Power<sup>42</sup> advocated cumarone resin as a bond for cold-molded abrasive wheels.

Investigations conducted at the author's laboratory have developed several types of cold-molding compositions of unusual character. For example, 20 parts by weight of acetone, 50 parts of formalin and 5 parts of sodium carbonate are mixed and heated under reflux. The resulting product is freed from water, dried, dissolved in alcohol and sodium or potassium hydroxide added (to catalyze the final reaction) together with the desired fillers.<sup>43</sup>

Another composition contains a binder which is the reaction product of glycerol with a natural resin, such as rosin or a copal, and an acid such as phthalic, citric, tartaric, malic, maleic or succinic. Diluents, softening or retarding agents may be incorporated with the binder.<sup>44</sup>

Still another type of binder for cold molding is the resin made by heating benzotrichloride and phenol until an oily condensation product has formed and reacting the oil with formaldehyde.<sup>45</sup>

**Fillers.** Fillers increase the strength, reduce shrinkage and improve resistance to shock or cold, as in the case of hot-molded articles. Asbestos is the customary material but it generally gives a rough surface. Long-fiber asbestos is best for

<sup>35</sup> E. J. P. C. de Jarny, U. S. P. 1,643,447, Sept. 27, 1927; *Brit. Chem. Abs.* B, 1927, 852. *British P.* 265,033, 1926; *Brit. Chem. Abs.* B, 1927, 259.

<sup>36</sup> T. C. Prouty, U. S. P. 1,453,726, May 1, 1923, to Proutyline Products Co.; *Chem. Met. Eng.*, 1923, 28, 1126.

<sup>37</sup> R. E. Coleman and F. J. Groten, U. S. P. 1,808,529, June 2, 1931, to Monowatt Elec. Corp.; *Chem. Abs.*, 1931, 25, 4370.

<sup>38</sup> H. C. Cheetham, U. S. P. 1,855,384, Apr. 26, 1932, to Bakelite Corp.; *Chem. Abs.*, 1932, 26, 3244. *French P.* 689,015, 1930; *Chem. Abs.*, 1931, 25, 1109.

<sup>39</sup> G. J. Votapek, U. S. P. 1,574,771, Mar. 2, 1926; *Chem. Abs.*, 1926, 20, 1500.

<sup>40</sup> J. P. Trickey and C. S. Miner, U. S. P. 1,655,233, Apr. 10, 1928, to Quaker Oats Co.; *Chem. Abs.*, 1928, 22, 1863.

<sup>41</sup> J. P. A. McCoy, U. S. P. 1,300,218, April 18, 1919; *Chem. Abs.*, 1919, 13, 1909.

<sup>42</sup> H. R. Power, U. S. P. 1,427,844, Sept. 5, 1923; *Chem. Abs.*, 1923, 16, 3738.

<sup>43</sup> Carleton Ellis, U. S. P. 1,514,505, Nov. 4, 1924; *Chem. Abs.*, 1925, 19, 710.

<sup>44</sup> Carleton Ellis, U. S. P. 1,541,330, June 9, 1925; *Chem. Abs.*, 1925, 19, 2277.

<sup>45</sup> Carleton Ellis, U. S. P. 1,793,310, Feb. 17, 1931, to Ellis-Foster Co.; *Chem. Abs.*, 1931, 25, 2312.

strength and resistance to shock but a smoother surface is obtained with a short-fiber grade and consequently a compromise is usually reached between strength and appearance by mixing the two. Wood flour may be added to improve the appearance but it reduces the heat resistance. China clay or other powdered inorganic fillers also improve the surface but diminish the impact strength. Talc is often added to minimize the abrasive effect of the composition on the mold and mica may be introduced to increase the dielectric strength.

**Methods of Mixing.** Pitch, asphalt, gilsonite, resin and other ingredients used to form the binder of cold-molding compositions are dissolved, with or without heat, in benzol or V. M. & P. naphtha in a kettle having an agitator to assist in forming the solution. Fillers are usually incorporated in small batches with the solution to obtain a uniform mass. With a short-fiber or powdered filler the amount of binder may be less than 25 per cent, but when long-fiber asbestos is employed it becomes necessary to increase the proportion of binder. When the batch is first removed from the mixer it is too sticky or tacky to mold and is therefore seasoned by exposure to air to evaporate part of the volatile solvent. If a drying oil is used, it is slightly oxidized by the air and this tends to reduce stickiness. After seasoning, the material is screened to proper size and allowed to remain exposed to the air until it has reached the best molding state. During this second stage the batch may be turned and blended several times a day to evaporate the solvent evenly. A rough test for molding consistency is made by squeezing a portion of the composition in the hand. If it remains compact, it is still too tacky, and if it crumbles to a powder it is too dry and must be blended with a fresh batch to moisten it. At the proper consistency it drops apart in a few lumps. When properly seasoned, the molding powder is placed in air-tight containers to prevent further evaporation and is stored in this manner until used.

**Method of Molding.** The shaping or molding of these compositions is conducted entirely by pressure without the aid of heat. The material, in the form of powder or granules, is weighed or measured by volume. The mold being properly secured in the press with the cavity at the bottom and the force at the top, the measured charge is placed in the mold cavity. The operator first closes the press slowly to drive air out of the composition and then gives the piece 2 or 3 sharp blows in rapid succession, by opening the press about 0.25-0.50 inch and quickly closing it. These blows are needed to set the material and give the article a good surface. The pressure exerted on the cross area of the piece ranges from 5 to 15 tons. The press is then immediately opened and the molded piece ejected. Difficulty arises at times from sticking to the mold and is generally caused by insufficient seasoning of the composition prior to molding. To avoid this, water applied directly to the mold may be used as a lubricant. The articles as they come from the press are rigid but soft and mechanically weak. They may, however, have a tough flexible surface film and in any event possess sufficient strength to withstand the handling necessary for the baking operation.

By the cold-molding process, production may range from 300 to 450 pieces per hour from a single-cavity mold, which is considerably greater than that secured in established methods of hot-molding in hand-operated molds.<sup>46</sup> An exact comparison of press output is difficult but it will suffice to call attention to the fact that molding is more rapid by the cold process. Cold-molded articles must be finished by a subsequent baking operation not required in hot pressing, where the process, except for the removal of the overflow fins and buffing, is completed on removal of the article from the mold.

<sup>46</sup> C. W. Rivins, *Plastic Products*, 1929, 5, 72.

**Baking.** Preparatory to baking, cold-molded pieces are arranged on perforated metal trays to permit free circulation of air and are dried for 24-48 hours at normal temperature before being heat-treated. The stoving or baking operation must be carried out very slowly to prevent blistering and deformation of the piece. The oven with its contents is gradually heated to expel the more volatile solvents at a low temperature and then the heavier and less volatile liquids as the temperature is increased. The size of the articles governs the time of heating, which ranges from 12 hours for small products to 96 hours for thick heavy pieces. The temperature is often raised to 250° or 300°C. If desired, the entire operation of molding and drying can be carried out within 24 hours but this increases the number of defective pieces considerably.

The inflammable nature of the solvents usually employed makes the baking operation a serious fire hazard. No open flame can be permitted in or about the oven, which is heated indirectly by hot air, circulated to maintain a uniform temperature. Means for venting are also necessary, particularly during the early stages of the baking period, to provide escape for solvent fumes and gases.

**Finishing.** The finishing treatment required often involves several operations and is an item of considerable expense. A piece may be knurled, machined or drilled before baking but the usual practice is to bake the pieces with even the overflow fins attached to reduce handling of the soft molded blank as much as possible. At times these fins cement themselves to the surface of the article during baking and form rough lumps difficult to remove. Final finishing of circular shapes is done in a lathe using a file as the tool. Flat pieces are finished on a sanding wheel. Two-part pieces are matched by smoothing the contact surfaces on a sanding wheel, and oversize is ground off in this manner.

A feature peculiar to cold molding is that flat molded surfaces in a plane at right angles, or nearly so, to the direction of pressure seldom or never take a good finish. On the other hand, rounded surfaces, in planes parallel to the direction of force, receive a high luster produced by the friction and heat accompanying the flow of the composition. For this reason flat surfaces are avoided and when circumstances require them they are, as a rule, milled, cross-hatched or treated in some similar manner to improve their appearance. Grinding marks can be removed and flat surfaces polished by buffing in the ordinary manner.

Richardson<sup>47</sup> has suggested that cold-molded articles of improved surface-finish result when the molding material is kneaded under pressure and extruded in the form of strips, which are then cut into blanks for molding.

**Molds.** The molds employed in the cold process, although similar to those for hot-molding, are built more strongly to withstand the high pressures and shocks to which they are subjected. Guide or mitre pins of rugged proportion are used to insure exact alignment. The mold surface is polished to about the same degree as that required for hot pressing. Molds are usually of the single-cavity, positive type; that is, the force is applied in such a manner that the full pressure is exerted on the entire charge of material at all times. This form permits the making of both oversize and undersize pieces and the charge must therefore be measured carefully. The molds also differ in that they must be so designed as to permit the composition, possessing little or no plasticity or flow, to be forced into all parts of the cavity. This sometimes necessitates making an article in 2 or more parts, a practice economically permissible (although it might be formed in 1 piece by hot molding) because of the increased output of cold molding.

In order to facilitate production and ease of removal without injury to the piece, either automatic or hand-operated ejectors are employed, the latter being

<sup>47</sup> L. T. Richardson, U. S. P. 1,944,464, Jan. 23, 1934, to Cutler-Hammer Mfg. Co.; *Chem. Abs.*, 1934, 28, 2082.

generally used with molds for small articles. New molds are usually made with small clearances and are then broken in on a press with a hydraulic pull-back, as the spring-actuated type has not sufficient power to open them. The severe abrasive action of cold-molding compositions shortens the life of molds and their

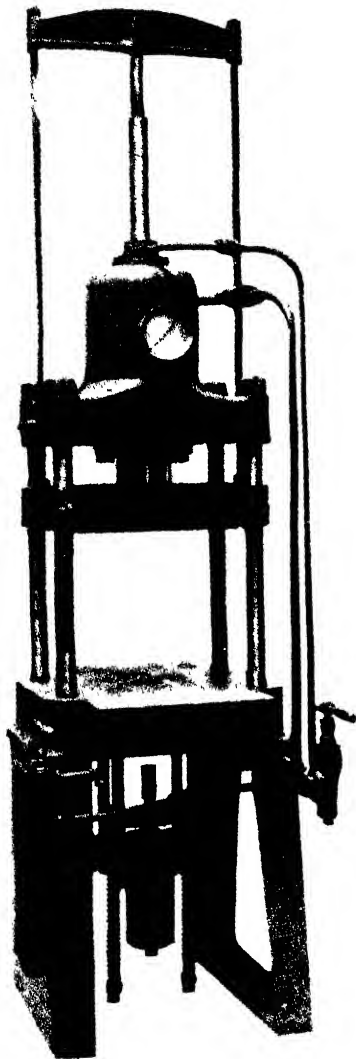


FIG. 175.  
Cold-Molding Press

*Courtesy Chas. F. Elmes Engineering Works*

maintenance is an important item of cost. Aside from injury resulting from negligence or accident, molds usually begin to show signs of wear after 10,000 pieces have been made, and an even shorter life is to be expected when the compositions contain an inorganic binder, e.g., sodium silicate. If dimensional requirements and finish are not important, as many as 30,000 to 40,000 pieces can be turned out before repairs are made. Wear is indicated by the appearance of flow

marks which multiply rapidly. The amount of metal lost can, of course, be readily determined by measuring a molded piece.

**Presses and Equipment.** The inverted ram type of hydraulic press is the one most extensively used in cold molding as it provides an immovable platen for the mold cavity and permits quicker and more convenient charging. The important features of a press are accurate alignment, sufficient pressure and suitable valve equipment adapted for high-speed operation. A small ram is essential when a high velocity is used to avoid the consumption of an excessive amount of pressure liquid and on this account a line pressure of 3000-4000 pounds per square inch is necessary. The presses are equipped with a spring or hydraulic pull-back, which permits rapid opening of the mold, an ejector mechanism and safety devices. Such presses are capable of exerting a total pressure of 10-25 tons. On the upward stroke the ejector is pushed up to any desired position and automatically released, permitting the ejector pin in the mold to reseat in position for recharging. An auxiliary hand lever is provided for holding the pin in place while removing certain articles, such as fuse plugs, which are molded with a thread that must be unscrewed. On presses employing more than 25 tons pressure a separate hydraulic ejector may be used. The one below the bottom platen in Fig. 175, is controlled directly by the secondary valve at the left side of the press. A three-way valve, providing for down-stroke, stop, or up-stroke, controls the application of the main pressure and, as it requires but little effort to operate, facilitates rapid molding. The machines may be equipped with a safety device to prevent accidental closing while the mold is being charged. To serve this purpose a secondary locking lever may be arranged on one side in such a manner that it must be depressed with one hand before the main operating valve, placed on the opposite side, can be opened. In this way, both hands are outside of the press before it can be closed.

To obtain maximum production the presses are equipped with quick-acting valves, made entirely of steel, as brass-seated valves wear out more rapidly under the cutting action of the high-pressure fluid. With steel fittings, oil is used in the hydraulic system to eliminate rusting. Pressure is maintained by means of pumps and accumulators, some of which are described in Chapter 67. The high pressures generally employed require that the hydraulic equipment be guarded against damage by shock absorbers placed at various points throughout the system to take up "water hammer."

## Chapter 67

### Molding Equipment

Molding is an economical and rapid method for the production of a large number of identical articles, but careful selection and design of equipment are as essential as is the use of the proper materials. This chapter is concerned with the types of molds, presses and accessories employed in the application of synthetic resins to the manufacture of molded articles.

**Types of Molds.** The mold is the tool which is used to give shape to the molding material while it is in a plastic state. Inasmuch as the initial cost of the mold represents a considerable proportion of the total expense involved, careful design is necessary. The number of pieces to be made, the material which is to be formed and the probable use to which the finished piece will be subjected must all be considered.

The various types of molds in general use differ chiefly in the manner in which they act upon the material to be formed and are classified as "flash" or "open" molds, "positive" or "closed" molds, "injection" molds and "blowing" molds.<sup>1</sup>

In the flash type the top rests upon the body of the mold, whereas in the positive form a tightly fitting plunger is forced into the lower section. In the former case an overflow channel must be cut around the cavities to collect the superfluous material or "flash." An injection mold is of the positive type but is empty when closed. The plastic material is introduced under pressure through a small port, thus requiring a composition which will stand preheating. The fourth type, the "blowing" mold, is used in the rubber, pyroxylin and glass industries for the production of hollow articles. The pressure on the molded article is exerted by a fluid, such as air, gas, steam or water. Hollow toys are commonly made from pyroxylin sheets or tubes in this manner. In general, this type is not used extensively in the fabrication of synthetic resin products.

Molds for the casting of thermoreactive synthetic resins are frequently made of a fusible metal such as lead. Such molds may be charged with resin before they are fully cold, and may be readily melted and reformed after each charge of resin if the mold is damaged in removing the piece.

Dies for extrusion molding are entirely different from the four types described above in that they give shape to the plastic material while it is being forced through them, and thus are suitable only for forming continuous moldings of uniform cross-section. The dies may, however, be solid, hollow or irregular in shape. These molds must be designed to insure free flow so that all material moves continuously and no "dead spots" are present.

Large multiple-cavity molds are used for the quantity production of radio tube bases, telephone mouthpieces and many small articles such as bottle closures. Sachse<sup>2</sup> has devised a mold for making pieces with re-entrant angles<sup>3</sup> by

<sup>1</sup> L. F. Rahm, *Plastics and Molded Products*, 1931, 7, 386.

<sup>2</sup> W. G. Alpeter, *Plastics and Molded Products*, 1932, 8, 199.

<sup>3</sup> W. Sachse, U. S. P. 1,687,797, Oct. 16, 1928, to Central Scientific Co.

forming these parts against a section of the mold which is removed with the piece and separated from it outside of the main cavity.

**Mounting and Heating of Molds.** The earliest forms of molds were heated by inserting them in a press between heated platens, or by resting the parts of the mold on a hot table. Cooling was effected by transfer to a cold surface or by cooling the entire mass. With the introduction of larger multiple-cavity molds the weight became so great that manual operation was impossible, and permanent mounting in the press was adopted. Improvement in the rate and economy of heating and cooling then became possible by heating the mold alone. When heating and cooling are both necessary, the mold is made hollow or cored, and steam and cold water are used alternately.

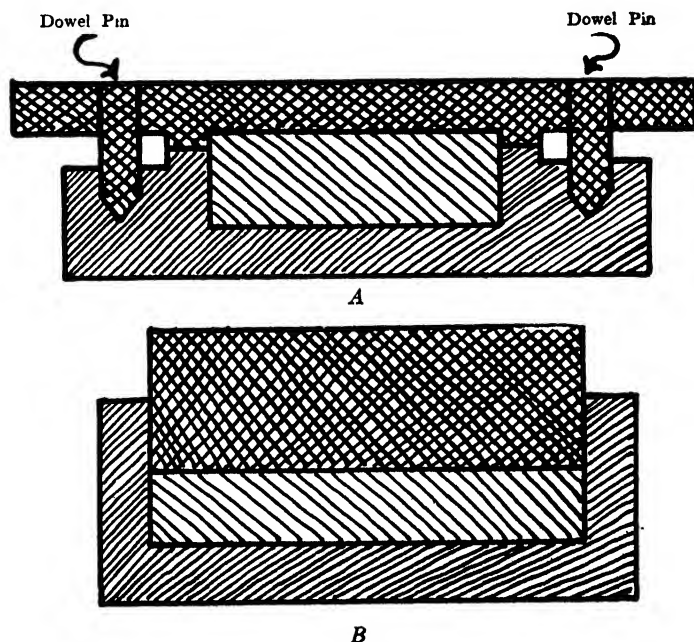


FIG. 176.—(A) "Flash" or "Open" Mold. (B) "Positive" or "Closed" Mold.

If heat alone is required, electricity or gas may be used. Electrically heated molds and platens have been much used and recommended, especially for small presses or for installations where high-pressure steam is not readily available.<sup>4</sup> This method is reported to be much more uniform than steam when used with thermostatic control, and is more economical when only one or two presses out of a battery are to be operated. Bell<sup>5</sup> has calculated that about five watts are required for each square inch of platen area in normal work with synthetic resins. Gas-fired platens for hot molding have been used for hard rubber telephone parts<sup>6</sup> and for phonograph records. High-pressure gas is almost a necessity, however, and special burners are required.<sup>7</sup>

The rate of heating and conductivity of molds are important, especially when

<sup>4</sup> R. M. Keeney, *Chem. Met. Eng.*, 1925, 32, 855. *British Plastics*, 1933, 4, 405, 443, 445.

<sup>5</sup> L. M. T. Bell, *British Plastics*, 1931, 2, 519.

<sup>6</sup> A. M. Lynn, *Plastics and Molded Products*, 1931, 7, 73.

<sup>7</sup> L. M. T. Bell, *loc. cit.*

both heating and cooling are necessary. The most important consideration is to obtain uniform temperatures on the various faces of the mold so as to prevent uneven curing and avoid warping or blistering of the molded product. Bronze dies are sometimes used when very rapid transfer of heat is desired, but trouble is often encountered from mechanical failure of the metal. Steel discs for phonograph records transmit heat rapidly enough to turn out two complete ten-inch shellac records per minute with both heating and cooling. This is accomplished by very complete coring of the dies.

**Powder, Tablet and Sheet-Stock Molds.** Molding compositions in powdered form are usually pressed in positive or closed molds. When briquettes, sheet-stock or tablets are employed a flash type of mold is very frequently used. The powder mold requires a cavity large enough to contain the required weight of composition and, in using a resin composition incorporated with a filler of wood flour or asbestos, it is customary to calculate the capacity of the cavity to be  $2\frac{1}{2}$  or  $3\frac{1}{2}$  times the final volume of the finished molded article. If a pre-form is employed the cavity may be the size of the finished piece. The advantage of this is readily apparent as it means less steel to heat up to molding temperature, lighter molds and lower cost in construction, in addition to the convenience and accuracy derived from the use of a tablet instead of a bulky powder which must be weighed for each molding.

The sheet-stock mold likewise requires a cavity of the same volume as the completed article, the sheet being packed tightly into the mold. However, sheet-stock requires some means of softening prior to loading in the press which calls for more equipment and labor.

**Inserts.** Inserts are parts of a finished molded article which are of different material from the molding composition but are set in place or positioned by the molding operation. Inserts may be of various metals such as steel, brass, copper, nickel or silver, or can be rubber, a molded resin part, a piece of laminated sheet or ceramic material. They are usually anchored to the mold in order to insure proper location and position after the mold is closed. This may be done by means of a pin in the mold which fits into a hole in the insert.

Care should be taken that the insert does not prevent the mold from closing tightly, otherwise a poorly molded article would result. This is important with metal parts which pass all the way through a piece. The simplest forms are always preferred, of course, especially those that can be made to close tolerances on automatic machines. For irregular pieces die casting has been used.<sup>9</sup> Peterson<sup>9</sup> has suggested wrapping metal inserts with several layers of cotton yarn before imbedding them in the resin. Metal overlays are often employed for decorative effects on laminated products of all kinds, such as table tops, trays, store-front panels, water coolers, and many other products.

**Materials Used for Making Molds.** Hardened steel is the most generally used material for molds. Since the cost of designing, fabricating and maintaining these tools is very high it is worth while in most cases to use hardened steel, and in special cases stainless steel. Although the initial cost may be considerably higher, the longer life of special molds and the lower cost of maintenance may overbalance the difference in cost of manufacture.<sup>10</sup> In cases where a relatively small production is required or where the design of a mold is of doubtful efficiency, soft steel is employed because slight changes may be made more easily. The unhardened steel mold, however, will require more frequent polishing and if used

<sup>9</sup> *British Plastics*, 1932, 4, 283.

<sup>10</sup> C. F. Peterson, *British P.* 359,353, 1930, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 436.

<sup>10</sup> *British Plastics*, 1931, 3, 71.



in constant production will have to be discarded in a comparatively short time. Gray iron castings may be used occasionally for molds when the peculiar or irregular shapes desired make machining difficult, but they are, of course, very brittle, cannot be well polished and have only a short life. In the manufacture of printing plates a "molded mold" made from synthetic resin with a thin metallic foil on the surfaces has been employed with satisfactory results. This type has been recommended also for various powdered materials.<sup>11</sup>

Alloy steels with special properties<sup>12</sup> have been used extensively in mold construction, and Hohl<sup>13</sup> has described some of these new applications. Steel for

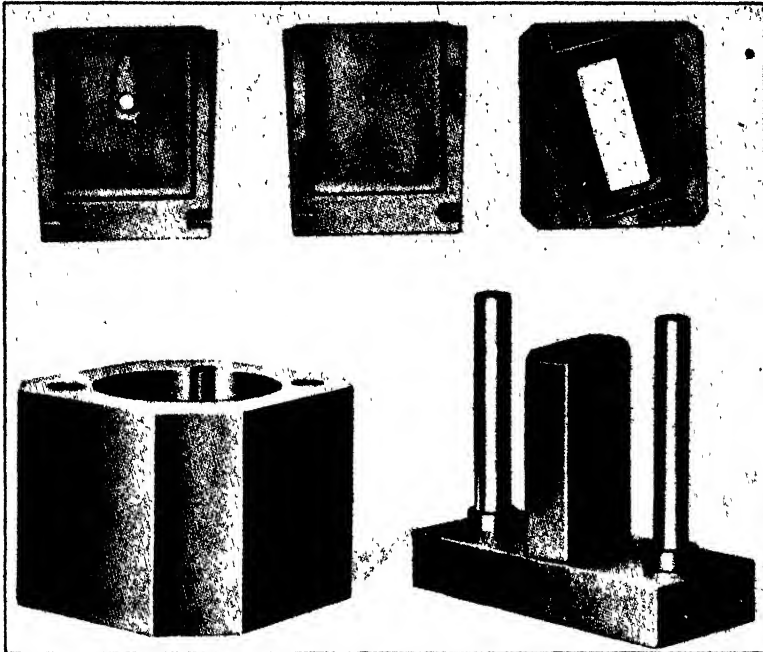


Fig. 177.—Illustrating Slightly Tapered Sides and Rounded Corners.

use in dies should, when hardened, have an ultimate strength in compression of 100,000-350,000 pounds per square inch. For extreme accuracy in molds it is essential to use steels which do not shrink or warp during hardening. This property is usually gained only at the expense of lower strength.

**Design of Molds and Molded Products.** There are no fixed rules for the design of molds although certain general principles have been pointed out.<sup>14</sup> Once the general design is decided upon there are a number of points which must not be overlooked if best results and lowest costs are to be realized, although it is often impossible to incorporate all desirable features. The most important considerations are given briefly below.

Sufficient "draft" or clearance must be allowed to permit removal of the piece

<sup>11</sup> L. M. T. Bell, *British P.* 271,192, 1926, to British Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1928, 22, 1696.

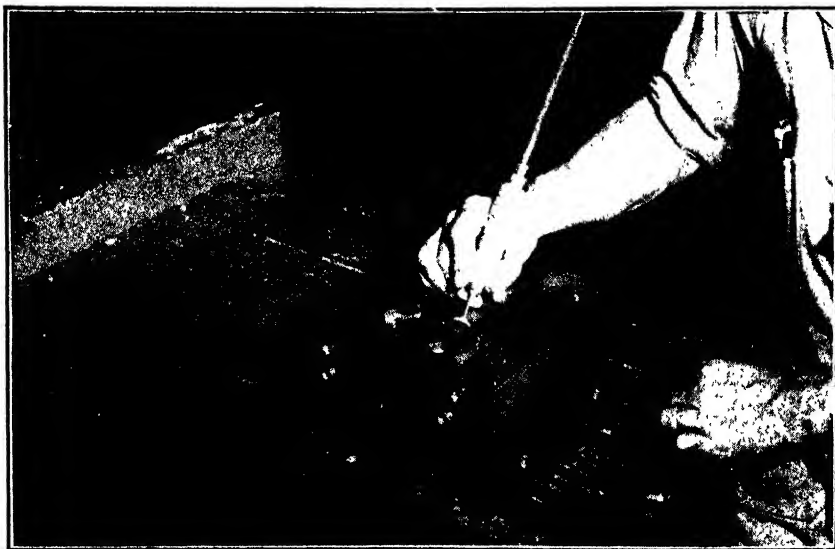
<sup>12</sup> A. C. Row, *British Plastics*, 1933, 4, 496.

<sup>13</sup> J. Hohl, *Plastics and Molded Products*, 1931, 7, 675.

<sup>14</sup> L. E. Barringer, *Gen. Elec. Review*, 1927, 30, 387. H. T. Richardson, *British Plastics*, 1930, 1, 430, 493, 544; 2, 32, 80, 120, 166. E. F. Bachner, *Plastic Products*, 1933, 9, 135.

from the mold. Thus, unless parallel sides are absolutely necessary, there should be, for hot-molded products, about 0.015 inch total taper per inch of length, or an angle from the parallel of  $\frac{1}{2}$  degree on each side, in the case of both outside and inside surfaces. Cold-molded goods require more, about 0.060 inch per inch or 2 degrees from the parallel. This is due to the fact that cold-molded products are still weak and fragile when removed from the mold.

All sharp edges or corners on the piece, into which the material has to flow, should be rounded off wherever possible, to allow better filling and less breakage. Similarly, edges or corners on the mold that come into sliding contact with another portion should be bevelled off, or protected, as by the use of dowel pins, to prevent mutual damage. For example, bevelled edges to be formed by a



*Courtesy Modern Plastics*

FIG. 178.—Machining a Mold Cavity.

plunger should be modified, as a blunt edge is much cheaper to maintain than a sharp one.

Loading and unloading of the mold should be as nearly automatic as possible. Frames or fixtures can be used to advantage on multiple-cavity molds. In general, the number of movable parts in the mold should be kept as low as possible, and the necessary operations in opening and closing should be made simple and foolproof. Dowel pins are of service in preventing the incorrect assembly of hand molds. Adequate knock-out devices should be incorporated even in the simplest hand mold.

Molds must be ruggedly built, and if possible, designed so that delicate parts are protected from mechanical injury whether caused by normal operation or by accidents. The weight of the mold, however, should be as low as possible, particularly in hand molds, for ease in manipulation, and in molds which are heated and cooled, because of the extra time, steam and water required to vary the temperature of the excess metal.

Sunken lettering should be used on the mold, giving raised figures on the piece. These can be readily stamped or engraved whereas a raised design requires removal of the adjacent metal which is much more difficult and expensive. Furthermore, raised letters are more easily damaged in handling and tend to increase maintenance costs.

Dimensions of molded pieces should not be closer than plus or minus 0.005 inch unless absolutely necessary, as unusual precautions are required to maintain closer limits. In large moldings a tolerance of 0.002 inch per inch of length can be attained for hot-molded pieces, and about 0.005 inch per inch for cold-molded goods.

Undercuts should be avoided in general, as they require a complicated mold, and make removal of the piece difficult since it is necessary to disassemble the mold completely in order to withdraw the article. Deep undercuts on the inside of a piece are even more difficult to produce, but shallow ones are used in many molded closures<sup>15</sup> for bottles and jars.

Holes and inserts should have their axes parallel to the line of pressing wherever possible. If this cannot be done, they should be limited to as few other directions as possible, in order to simplify the operation of removing the pins forming the holes. Very small holes, requiring slender pins, are difficult to make. Therefore pin lengths should be limited to two diameters if possible.

Thin sections of any kind should be avoided, especially when heavy walls are also present. Thus, long holes closely spaced, or holes nearer the edge than one-eighth inch are objectionable. Large holes with square corners near an outside surface are likely to cause breakage, and great reduction in cross-section in any plane should be guarded against for the same reason.

Round sections, capable of production on a lathe should be used where practical, because of the lower cost of machine work and the greater ease of molding.

Threads should be as bold as possible, coarse, multiple threads being used frequently on jars and closures to give quick sealing action. Rings or plugs for molding threads can often be discharged with the piece and unscrewed by machine outside of the mold.<sup>16</sup> Knurling should be bold, and in straight lines parallel to the direction of removal of the piece, facilitating operation. Knurling at right angles, or diamond knurling, requires a three-piece mold in order to prevent damage during stripping.

Multiple-cavity molds should be made so that one damaged unit can be replaced without impairing the remainder of the mold. This can be done, for example, by the use of a chase, or major mold which holds the independent molding units, as in molding telephone mouthpieces, described by Alpeter.<sup>17</sup>

**Shrinkage Allowance.** Molded articles may be made to very exact dimensions if the shrinkage of the molding composition is taken into account. The ideal preparation should possess just sufficient shrinkage to allow easy removal of the articles, but at the present time, none are perfect from this standpoint. Those of the phenol-formaldehyde type have a contraction of 0.004-0.009 inch per inch of length. This variation must be calculated when a box with a tightly fitting lid is to be designed, and likewise when pieces must exactly fit into a standard sized cavity in a piece of apparatus. The allowance depends on the material used, and in addition, the contraction will be greater when the piece is removed hot than when it is cooled in the mold under pressure. Shrinkage will depend also upon the pressure at which a piece is molded. There is a tendency for

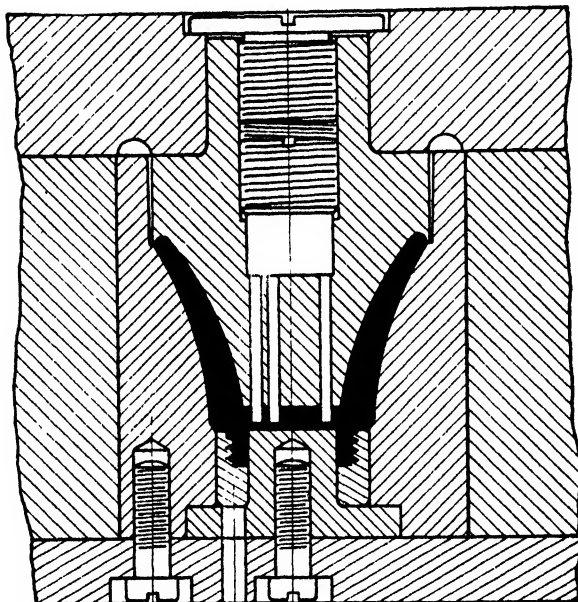
<sup>15</sup> *Plastics and Molded Products*, 1931, 7, 140.

<sup>16</sup> W. G. Alpeter, *Plastics and Molded Products*, 1932, 8, 199.

<sup>17</sup> W. G. Alpeter, *loc. cit.*

molded pieces to shrink away from the mold cavities, and onto the mold plungers. This is particularly troublesome in the molding of large, deep parts, such as radio cabinets, where there is liability of breakage if the material cools unduly before it is removed from the plunger. Advantage has been taken of high shrinkage to unite parts inseparably. In one case knobs on the tops of tobacco jars<sup>18</sup> have been molded, cooled, and inserted into a cavity in the cover of the jar before the latter had cooled after molding.

The accurate design of molded threads has been discussed by Richardson.<sup>19</sup> It is apparent that the thread will shrink both in diameter and in length, so that



Courtesy Western Electric Co.

FIG. 179.—Cross-section of a Single Telephone Mouthpiece Mold. Three distinct parts are shown: the punch which forms the bell mouth and grill holes, the cavity shaping the exterior and the loose insert that forms the threads.

the size and the pitch both change. This effect is noticeable when a molded and a cut thread must mesh exactly for lengths greater than two diameters. Such cases are rather rare, and when they do occur the difficulty can often be met best by the use of metal inserts. Shrinkage may be readily determined by comparing the dimensions of the cold mold and the cold piece. Similar procedures and shapes will give check figures, but marked variation in either is likely to yield different results.<sup>20</sup>

**Fabrication of Molds.** A well-equipped machine shop is, of course, necessary for the manufacture of molds, and in addition, modern practice requires special hobbing tools. It is usual to do all the machining operations required in the mold with an automatic machine, electrically controlled so that the cutter follows the contours of a master mold or template. The master forms employed may be

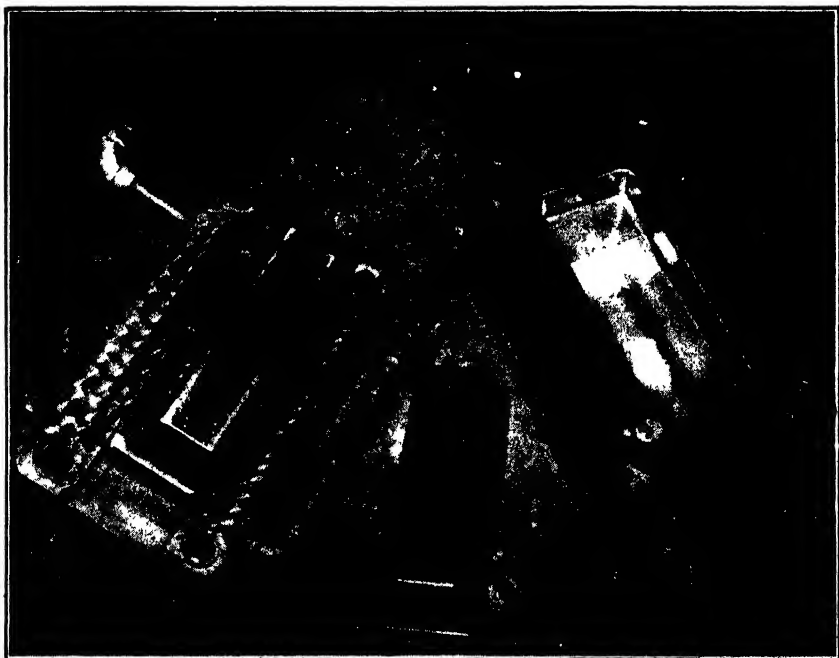
<sup>18</sup> *British Plastics*, 1931, 2, 396.

<sup>19</sup> H. T. Richardson, *British Plastics*, 1930, 2, 166.

<sup>20</sup> Values for the contraction of several types of molding preparations are given by H. T. Richardson, *loc. cit.*

very simple. Light metal templates or solid masters of wood, cement, lead or other easily formed material including molded synthetic resin compositions are entirely adaptable for the heaviest cuts. An old or broken mold may be used as a master to make new ones, or a finished article may be used as a master to make a hob, from which molds may be made. Gleason<sup>21</sup> has compared the details of the jig-boring and the "button" method of locating holes accurately, suggesting that the latter procedure is quicker, more accurate and cheaper.

Lynn<sup>22</sup> has given a detailed description of mold making for a hand-set telephone handle which has very irregularly curving surfaces. Two hardened steel



*Courtesy Monsanto Chemical Co.*

FIG. 180.—A Typical Mold Assembly.

master hobs were first made, duplicates of the upper and lower part of the hand-set, and were used to check each final mold. Master cavities were made from the hobs and the molds cut from these cavities by automatic machines were finished by hand to match the master hobs.

**Hobbing of Molds.** The hobbing of molds has gained great prominence in mold production.<sup>23</sup> This method, originally known as hubbing and sometimes called die-sinking, is really the forming of the steel mold itself by pressing a hardened steel hob or hub into a soft steel blank under hydraulic pressure. The procedure is similar to that used in the production of metal coins but should be distinguished from the hobbing of gears, where a cutter is employed.

Hobbing is particularly valuable where a number of identical molds or mold-cavities must be made. The process can be used to make molds which cannot be

<sup>21</sup> L. S. Gleason, *Plastics and Molded Products*, 1931, 7, 658.

<sup>22</sup> A. M. Lynn, *Plastics and Molded Products*, 1931, 7, 73.

<sup>23</sup> *British Plastics*, 1930, 1, 404.

machined and polished by any other means. For example, in the manufacture of a certain fountain pen barrel, the mold is over four inches deep, with twelve polished flat surfaces or flutings running lengthwise, while the inside diameter varies from 7/16 inch to about 1/4 inch. The several hobs of increasing length which were used for this were shaped and polished with relative ease, but the mold cavity made by them could not be machined directly.

The hobbing press thus becomes one of the most important tools in a modern mold shop. The hydraulic pressures required are high, 6000 pounds per square inch and even more being usual, and the press capacities range from 200 to 2000 tons total pressure. The platens are of solid steel, not equipped for heating or cooling.

The hobs are made by regular machine shop methods to duplicate the desired article, or that part of it which is to be hobbled. Sometimes two or more different hobs may be used in the making of one mold. The steel used must be very tough, and capable of being hardened and polished. In the United States a good grade of tool steel with 0.80 to 0.90 per cent of carbon is generally preferred,<sup>24</sup> although some molders favor alloy steels. In England, an alloy with 12 or 13 per cent of chromium and 2 per cent of carbon is widely employed.<sup>25</sup> The steel used for the molds must have a very high elastic limit, and must flow under pressure without crumbling or splitting. Low carbon steel or even very soft pure Swedish iron is generally employed where deep cavities are to be hobbled, but well-annealed carbon or nickel-chromium steels can be used for shallow parts.<sup>26</sup> Such stainless steels are sometimes hobbled<sup>27</sup> although they present difficulties.<sup>28</sup>

The hobbing operation is usually carried out by means of a hobbing shell or ring.<sup>29</sup> The hob fits in the top of this, and the steel mold blank fits in the bottom. The blank should have about 70 per cent as much metal removed from the sides, edges, or bottom as will be displaced by the hob. The exact shape of the piece before hobbing depends upon the size and shape of the impression and upon the judgment of the operator, but the surface exposed to the hob should be machined smooth, polished and lubricated with oil before the hob is placed in position. Pressure of 100-200 tons per square inch is applied, forcing the hob into the mold blank. The soft steel flows out below, and the upper surfaces take the exact shape of the hob, including its finish. Pressing is continued until the required depth is reached, or until the force required becomes excessive. The hob and mold are then pressed out of the hobbing shell, when the hob can usually be removed from the mold without difficulty. In hobbing deep impressions it is necessary to anneal the mold a number of times to overcome hardening caused by cold flow. Some work on hobbing molds in hot metal has been reported,<sup>30</sup> but this is not common practice.

**Hardening and Finishing of Molds.** Steel molds may be made by conventional machine shop methods or by hobbing, but for best results they all require hardening. The case- or pack-hardening process may be used for low-carbon steels<sup>31</sup> and quenching in oil or water for tool steels. Trouble is often experienced from the warping or shrinking of steels during treatment, but this can be overcome by employing special non-shrinking oil-hardening steels,<sup>32</sup> usually at the

<sup>24</sup> H. Chase, *British Plastics*, 1932, 3, 522, 562.

<sup>25</sup> *British Plastics*, 1931, 3, 71.

<sup>26</sup> J. Hohl, *Plastics and Molded Products*, 1931, 7, 675.

<sup>27</sup> H. Chase, *loc. cit.*

<sup>28</sup> *British Plastics*, 1931, 3, 71.

<sup>29</sup> H. T. Richardson, *British Plastics*, 1930, 2, 166.

<sup>30</sup> A. C. Row, *British Plastics*, 1933, 4, 496.

<sup>31</sup> E. F. Bachner, *Plastics and Molded Products*, 1933, 9, 135.

<sup>32</sup> J. Hohl, *Plastics and Molded Products*, 1931, 7, 675.

expense of ultimate tensile strength and elongation. Alloy steels,\*\* containing small amounts of aluminum, chromium, molybdenum and carbon, show low shrinking and warping and take a fine polish which is somewhat corrosion-re-

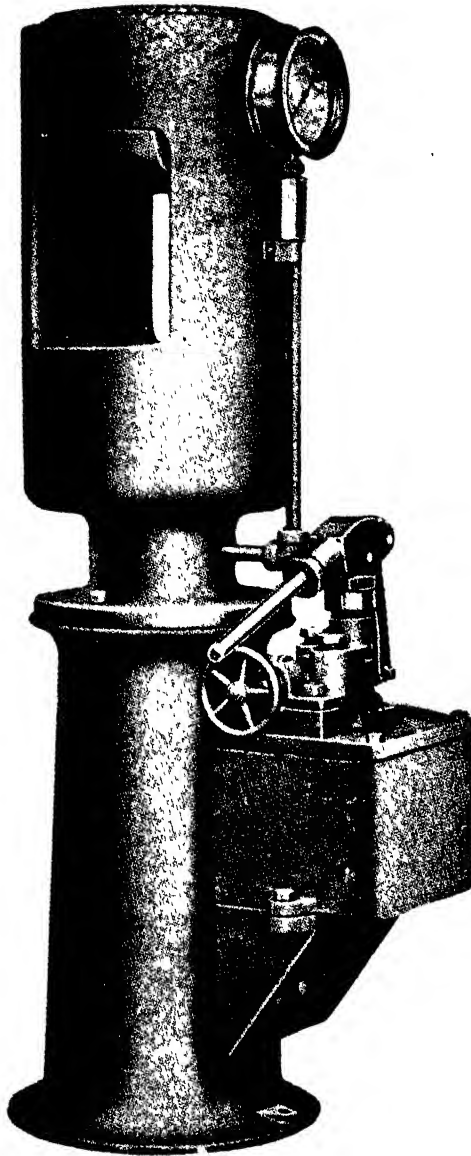


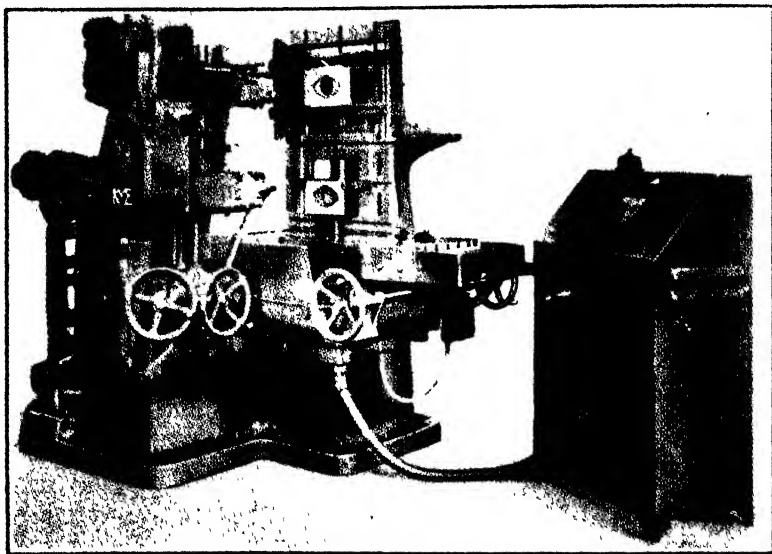
FIG. 181.  
Hobbing Press.

sistant. They are hardened by heating at about 900-1100°F. (480-590°C.) in ammonia gas and are cooled without quenching. The long time required for this operation has apparently limited their use.

\*\* *British Plastics*, 1931, 3, 71.

The final operations on molds of all kinds are finish-grinding and polishing with emery or rouge and oil. The polishing of the hardened steel mold is chiefly a tedious hand operation and a large proportion of the cost of molds is represented by this work. In connection with the design of molded products some designers are now calling for special dull finishes on the molds, or on certain areas of them, in order to give contrast with the brightly polished sections.<sup>24</sup>

**Repairs and Maintenance.** Careful handling of molds by the molder and the use of hardened steel molds greatly reduces the cost of repairs and general maintenance, but all molds must be kept well greased when not in use (to prevent



*Courtesy Pratt and Whitney Co.*

FIG. 182.—Automatic Machine Designed to Produce Molds from a Master Template.

rusting) and free from abrasives which would mar the surface. Actual breakage of molds is not common but damage may result from many causes, such as careless handling or from foreign material in the composition. Multiple-cavity molds are usually constructed so that the block containing a damaged cavity can be removed and a spare mold inserted. Provision is often made on the loading frame so that a damaged section need not be changed, thus allowing the good parts of the mold to be used until repairs can be made conveniently.

**Molding Presses.** The function of the press in the molding of plastic materials is to exert and hold the high pressures which are necessary to flow the materials and compact them into a solid, non-porous mass. The earlier molding presses utilized the principle of the lever, the screw, or the toggle, but as higher pressures were called for, the hydraulic press came into almost universal use. It was found to be the best means of converting the high speed and low pressure power of the prime mover into high pressure and relatively low velocity required in the pressing of plastic materials. Mechanical molding presses are used in certain cases, however, as in the shaping of preforms from loose molding powder.

<sup>24</sup> F. E. Brill, *Plastic Products*, 1933, 9, 54.



The discovery of the basic principle of the hydraulic press is generally credited to Pascal (about 1653). The essential parts of the machine are a cylinder within which is fitted a ram, the former being a part of an open frame. The ram is forced out of the cylinder by means of a fluid pumped into the cylinder. The top of the ram is equipped with a flat surface or device known as a platen and the under side of the head of the press frame opposite the end carrying the ram is furnished in similar fashion. Thus, by the introduction of fluid to the cylinder, the movable platen approaches the fixed platen and a mold placed between them is subjected to heavy pressure. Water is the liquid generally employed and this is forced into the bottom or end of the cylinder exerting pressure between the platens equal to the area of the ram times the unit pressure of the fluid. In hot presses the cylinder may be copper-lined and gaskets are placed so as to be as remote as possible from the source of heat. Cooling or chilling presses are usually equipped with a "U" packing, which is set in an annular groove near the mouth of the cylinder and so arranged that an increase in fluid pressure expands the packing against the surface of the ram and the cylinder walls, and thus becomes tighter as the pressure increases.<sup>35</sup>

**Platens.** In presses to be used with hand molds, the platens may be cored for the circulation of steam and water for heating and cooling. In some cases where cooling is not required, the platens may be heated by gas burners or by electric heating units built in as an integral part. As mentioned above, steam heat is by far the most frequently used, especially where a number of presses are operated together. The high heat of condensation gives very quick heating, and overheating is impossible when pressure is controlled. In presses equipped with direct-heated molds, the platens are usually drilled or slotted to accommodate the fixtures necessary to secure the mold. Frequently a support, or "bolster," is used allowing space for the knock-out mechanism for ejecting the molded pieces.

Mechanically, the press should be designed to keep the platens in exactly parallel planes to prevent possible damage to the molds or to the press itself. Where hand molds are employed, the surfaces of contact on both mold and platen should be as flat and clean as possible to insure good contact, and thus give the quickest possible heating and cooling. Some means must also be provided for opening the press after it has been closed under pressure. The weight of the cylinder and platen is occasionally relied upon or springs may be provided, but generally auxiliary hydraulic "pull-back" cylinders are used. Separate hydraulic cylinders may be provided to operate ejectors or remove the pieces when cured.

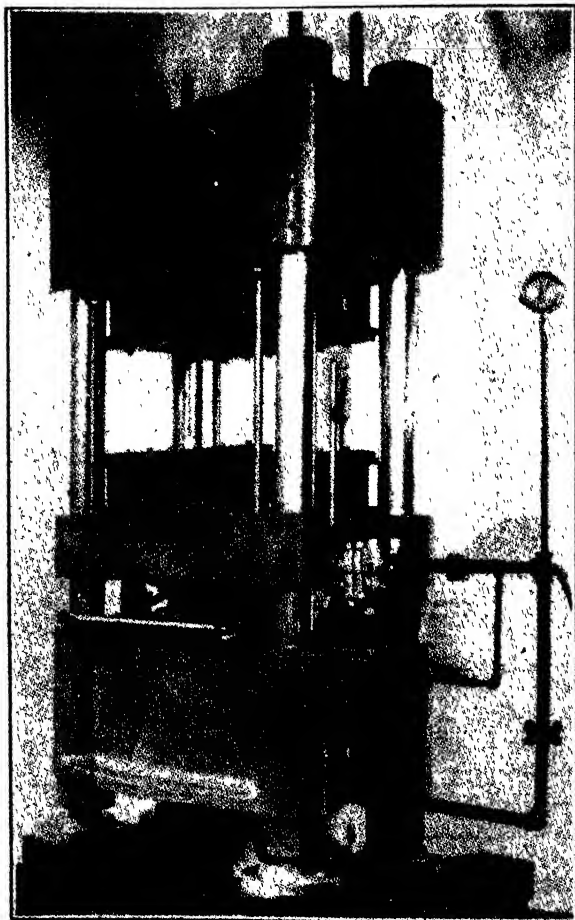
**Rod and Rodless Presses.** The rodless press is the simplest form, the head, sides, and cylinder being cast in one piece of steel. The cylinder is lined and bored, and the head faced at one setting, thereby insuring that the faces are perpendicular to the bore. The rigid sides or uprights permanently maintain this condition. Variation in the size of the opening can be obtained by inserting parallel spacer rings between the head of the press and the top platen. The rod press may be distinguished by the adjustable steel uprights which support the head instead of the cast steel sides used in the rodless type.

The inverted-ram press differs from those previously described in that the ram and cylinder are placed at the top, applying the force downward rather than upward. Provision may be made for a hydraulic pull-back above the main cylinder, which pulls the platen upward when the pressure is released. Cold-

<sup>35</sup> For a detailed account of packing materials and methods, see "Hydraulic Engineering," E. F. Houghton & Co. Research Staff, Philadelphia, 1926.

molding presses are frequently of this inverted-ram type so that the operator will have the lower mold always at the same level for quick loading and discharging.

Presses used for forming laminated material are usually of the rod type, provided with multiple steam-heated platens. With such equipment the impregnated fiber may be placed between polished steel plates and cured under high pressure. Various finishes may be obtained by the use of polished, sand-blasted,



*Courtesy Dunning and Boschert Press Co.*

FIG. 183.—Rod Press.

or engraved plates, and the color or design may be changed by using different top and bottom sheets on each pile of paper or fabric. In the design, installation and operation of multiple-platen presses great care is necessary to ensure equal and uniform heat on all platens so that warping will be reduced and equal cure will be obtained in all openings. This requires uniform piping to each platen, and care to prevent clogging or filling with water. Either swinging or sliding joints may be used in the steam and exhaust pipes.

**Tilting-Head Molding Presses.** The tilting-head press is particularly adapted for work where both sections of the molds must be readily accessible, especially when inserts must be placed in both parts. This construction also allows the stroke of the ram to be shortened materially, effecting a considerable saving in the amount of pressure liquid required. A variation of the tilting head press employs a sliding lower platen for still great accessibility. In another type a rotating frame has been added to the lower platen, together with heating and cooling surfaces so that the mold temperature may be varied by changing from a hot to a cold station.



FIG. 184.  
Tilting-Head Press Fitted  
with Multiple Mold for  
Production of Telephone  
Mouthpieces.

*Courtesy Western Electric Co.*

Lynn<sup>26</sup> has given operating details for tilting-head presses, and Alpeter<sup>27</sup> has also described and illustrated the special fixtures used for loading and unloading when molding telephone mouthpieces. The phonograph-record press is usually of this form, as it is necessary to inspect the upper mold, or matrix, and to place labels in position.

**Angle Presses.** Molded articles with threads, bosses or panels on their exteriors necessitate split molds held together by a bulky chase or retaining ring unless a special press is used. A large amount of heat is required to effect the cure in these heavy molds, and quantities of high-pressure water are needed to force the rams through a long travel. In addition, the whole operation is expensive because of the time involved in handling. The angle press has greatly facilitated work of this description. The usual form employs a horizontal ram to close and open the bottom half of the mold, so that a great proportion of the manual work is eliminated. Presses of this kind have been used in the manufacture of telephone receivers.

<sup>26</sup> A. M. Lynn, *Plastics and Molded Products*, 1931, 7, 73; *Mechanical Engineering*, Oct. 1930.

<sup>27</sup> W. G. Alpeter, *Plastics and Molded Products*, 1932, 8, 199.

**Hydraulic Pressure Systems for Presses.** All hydraulic presses require some source of pressure to close the press and hold it in this position during the period of curing. The first equipment used for this purpose was a hand pump, generally attached to the press. This was extremely slow, as a pump capable of giving the high pressure required can deliver only a very small quantity of water. Combination hand pumps have been developed, with the addition of a larger high-speed cylinder, for use when the power required is negligible, as in the idle part of the stroke while bringing the plunger into position. Pressure is main-

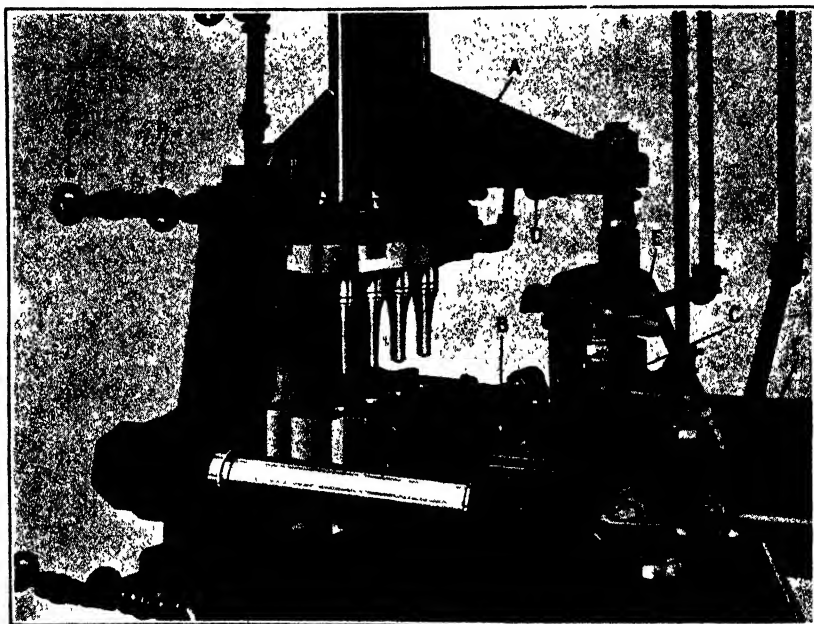


FIG. 185.—Angle Press. In this illustration the horizontal ram *B* of the press is closed and the vertical ram *A* is in open position, leaving the mold ready for charge of molding composition prior to pressing. The valves *G* and *H* control the steam and water for heating and cooling the molded parts. Valves *D* and *E* control the vertical ram and *C* and *F* control the movements of the horizontal ram.

tained by closing the valves, but any leakage or shrinkage of the molding material reduces its intensity.

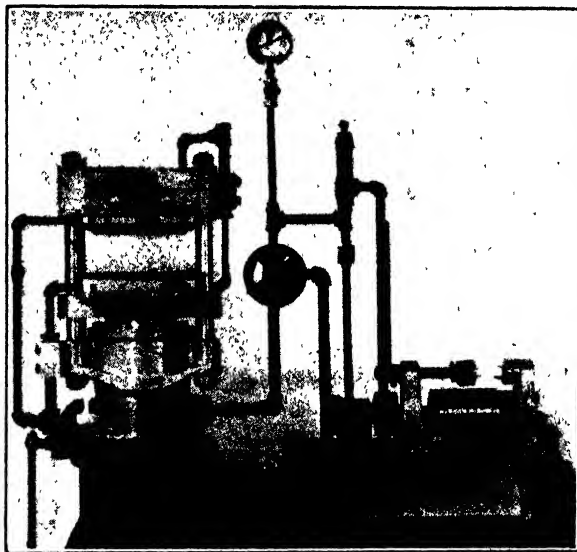
Mechanical power pumps are now employed almost exclusively. The first of these was the reciprocating pump often built with two sets of cylinders and an automatic device to change from low pressure to high pressure when the resistance of the press increased. A by-pass, or relief valve, is necessary to prevent damage to the equipment if an accumulator is not used. Such small reciprocating pumps were sometimes arranged one to each press, giving a convenient, self-contained unit of press and pump. This proved to be inefficient, however, and large hydraulic pumps with accumulators are much more generally used where a number of presses are operated together. The pumps of greater capacity are mostly of the multiple cylinder type, either vertically or horizontally mounted, and usually are fitted with individual motor drives and reduction gears. Steam pumps have also been employed.

An accumulator is a reservoir which is added to a hydraulic system to allow flexible operation. It will maintain pressure for a short time even when the pump is turned off, and is also capable of furnishing large quantities of water for a short period of time. An accumulator of some kind is installed on almost every high-pressure system, and may be used on an auxiliary low-pressure system, although low-pressure lines are often supplied by centrifugal pumps, thus making them flexible and efficient, even without the addition of an accumulator.

**Types of Accumulators.** In the most common type of accumulator the pressure is maintained in the system by a dead weight, usually of metal, supported on a ram which is free to move up and down in a cylinder. The total weight supported per unit area of the ram determines the pressure in the system. When the pump is operating, the ram and weights are raised, falling when water is

FIG. 186.  
Single-Opening Curing  
Press Fitted with Indi-  
vidual Belt-Driven Pump.

*Courtesy R. D. Wood and Co*



withdrawn. This motion of the accumulator may be utilized to operate the pump controls, opening a by-pass valve which allows the pump to run without load when the weights reach the top, and closing the valve again when approaching the bottom of the stroke. The capacity or volume of the accumulator cannot be readily changed. The pressure is constant, whether the weights are at the top or near the bottom, and can only be altered by varying their mass.

The design and capacity of the accumulator and pump depend upon the number of presses operated, the frequency of operation, length of stroke on hydraulic pressure and many other factors. Care should be taken that the accumulator is sufficiently large to avoid rapid drops of the weights, as the inertia of the falling mass will cause severe hydraulic shocks in the system. A larger ram is more expensive and requires heavier weights but a shorter stroke for the same capacity.<sup>28</sup>

The hydropneumatic type of accumulator may be used when the hydraulic pressure must be changed frequently, or when solid foundations are not available for a weight-loaded type, as for example, on the upper floors of buildings. This

<sup>28</sup> W. F. Lent, *Plastics and Molded Products*, 1931, 7, 671.

type reduces hydraulic shocks also, as the weights on the hydraulic ram are replaced by air pressure. The air may be at equal pressure, acting on a ram of the same diameter, or of lower pressure on a correspondingly larger ram. Tanks, or "air bottles," serve to increase the volume of air under pressure, and thus reduce the variation in pressure from one end of the stroke to the other. A tail-rod attached to the floating piston projects from the water end of the cylinder and controls the pump in the same manner as with a weight-loaded accumulator.

In another type of hydropneumatic accumulator the air pressure is lower than the hydraulic pressure, balance being maintained by the use of cylinders and



FIG. 187.—  
Placing Preformed Tablets in the Press.

*Courtesy Bakelite Corp.*

plungers of different sizes. In this case the plunger on the air cylinder is attached to the hydraulic cylinder, forming the moving part between the stationary air cylinder and the stationary hydraulic plunger, and replacing the floating piston in the equal-pressure type. The pressure ratio is the inverse of the ratio of the areas of the two cylinders. The capacity is that of the hydraulic cylinder, and operation is exactly similar to that of a weight-loaded accumulator. The percentage change in pressure is proportional to the volume of the air tank attached to the air cylinder. Installations have been built using steam pressure instead of air pressure. The differential cylinder principle is also commonly used in the pressure "intensifier" in which case a liquid is used on both low and high pressure sides. The volume which can be delivered is small, but tremendous pressures can be attained.

**Mechanical Power Presses.** As stated at the beginning of this chapter, the earliest presses used for molding were mechanical in principle. The hydraulic press is now widely used, but the older types have been adapted to molding work and are largely used in the making of preforms.<sup>60</sup> The mechanical molding press has all the advantages of a self-contained unit, and can be located without reference to accumulators or hydraulic piping. By the use of electric or gas heating

FIG. 188 —

Removing Molded Closures from  
the Press Ready for Finishing.



*Courtesy Bakelite Corp.*

it can also be made independent of steam lines, or high-pressure steam boilers. More presses can be added at any time without danger of overloading existing pressure or steam-heating equipment, which is a consideration in planning accumulator systems.

Several types of presses are available, some using the toggle principle, with pressures up to 200 tons, some a double lever system by which pressures of 800 tons are developed and others a combination of cam and toggle for shallow molding, and a rack and pinion for deep molding where longer strokes are necessary. These presses may be operated manually, semi-automatically or automatically. Mechanical toggle presses, belt-driven from line shafts, are used to some extent in phonograph-record pressings operating at lower pressures than hydraulic presses in the same work.<sup>60</sup>

An unusual type of mechanical press, using the impact power of a falling

<sup>60</sup> See Chapter 68 for preforms and preforming presses.

<sup>60</sup> See Chapter 68 for details of record pressing.

weight to give the required pressure, has been described by Bradley.<sup>41</sup> It is reported that good results have been obtained from a cold-molded type of material by placing the dry powder in the cold mold, compacting slightly to remove air, and then, by dropping a weight with an energy of about 1200 foot-pounds on the plunger, compressing the material into a solid article, firm enough to withstand the handling of subsequent baking treatment.

**Automatic and Semi-Automatic Presses.** Equipment, capable of producing molded articles with little or no attention from the operator, is the result of the demand for greater production and lower costs. The semi-automatic devices with which the operator charges the molds, starts the automatic cycle, and removes the finished pieces are, however, much more common than fully automatic equipment. Controls of this sort can be attached to either hydraulic or mechanical presses. Molds are mounted on the platens, usually on so-called "bolsters" or die carriers, which allow space for the operation of the ejector pins in the removal of the finished piece.

The ejector mechanism may be operated by the opening of the press or by independent means. In old types it was sometimes necessary to close the press after ejection in order to return the knock-outs to the proper position for re-loading. Independent ejectors are usually limited to hydraulic presses, where separate cylinders may readily be installed to actuate them.

**Timing Mechanisms.** The automatic type of press is usually controlled by motor-driven valves. Several presses in a group may be operated from one timing control as is done in phonograph record pressing. The cycling control may be automatic so that the presses open and close continuously. The operator is merely required to place labels and stock in position, and remove the finished record and flash. If he should be late, the press goes through a cycle without any stock and of course produces no record. Another method used is to operate a timing lineshaft continuously, but to let the operator start the cycle for each press, for example, by closing the head of the press or by pushing a connecting lever. This has an advantage in that a slow operator does not miss a complete cycle, but can start when ready. He can control the start but cannot otherwise change the cycle. In both this system and the automatic timing described above, the total cycle time can be varied by changing the speed of the line-shaft drive, but the mechanism at each press must be altered in order to change, for example, the ratio of heating to cooling time.

Signal and recording instruments are available in various combinations,<sup>42</sup> which may be applied to molding presses in any way desired. One installation has a control which is set for the minimum time necessary to insure water-resistance in urea-formaldehyde products. If the operator opens the press too soon a light is turned on and a bell rings to attract the attention of the foreman. Heat indicators are available which show by colored lights the temperature of the press. Recording controllers will indicate the exact time of opening and closing of the press while operating automatically at any time of cure desired.

The use of automatic molding machines is warranted only in cases of large and continuous production with little or no change in the design of the product, as for example radio tube bases. In style goods, such as lipstick cases, cigarette holders and novelties of all kinds, where designs are changed frequently, or production is likely to be intermittent, the initial expense is likely to be greater than the saving.

<sup>41</sup> H. L. Bradley, U. S. P. 1,793,435, Feb. 17, 1931; *Plastics and Molded Products*, 1931, 7, 521.

<sup>42</sup> M. F. Behar, "Manual of Instrumentation," Instruments Publishing Co., Pittsburgh, Pa., 1932-1933. This is a complete set of books on instruments and their use. Part I is general; Parts II and III cover temperature and humidity measurement and control; Part IV includes information on cycling control.



# Chapter 68

## Methods of Molding

In the actual molding operation as applied to synthetic resins there are so many procedures and minor variations in process, that it is desirable to classify the field to correlate the differences, as far as possible, and to indicate the advantages of the methods.

The first requirement is a mold which gives the material the required shape, finish and size.<sup>1</sup> The composition must then be softened, made to fill the form perfectly, hardened, and finally separated from the mold. Usually certain finishing operations are required, such as trimming or polishing rough edges (see Fig. 189), but these, although adding somewhat to the cost of production, are relatively unimportant.

### TYPES OF MOLDING

The methods of carrying out these various steps in the molding process, the material used and the characteristics of the finished article determine the type of molding. The simplest operation with synthetic resins is the casting of a non-reactive material, and the most complicated is probably the hot molding of a thermoreactive preform which requires cooling after curing. Table 68 (see next page) classifies the various types, some of which have names that are often misleading to one not familiar with that particular branch of the plastic molding industry.<sup>2</sup>

**Casting of Synthetic Resins.** The simplest operation, that of casting a fusible resin, is frequently used where sealing or luting is required, as in mounting radio transformers. Grant and Farren<sup>3</sup> have described a sulphur-cumarone resin-filler mixture for sealing electrical apparatus. Non-reactive cast resins are not extensively used, because, if they have a sharp enough melting point, they generally tend to have the brittleness associated with crystalline materials rather than the toughness of colloids.

At one time the casting of phenol-aldehyde resins (with subsequent reaction at relatively low external pressure) was deemed to be commercially impractical, but now it is used to procure colored products which readily permit machining. The resin is allowed to react under controlled conditions until it is almost converted to the insoluble stage whereupon the hot, gelatinous mass is poured into warm lead molds and allowed to harden by further chemical reaction at controlled temperatures.<sup>4</sup>

A method of casting multi-colored laminated materials has been described by Helfreich.<sup>5</sup> Plates of hardened resin, formed by either casting or cutting, are supported in a mold and more resin which may be of a different color is cast between

<sup>1</sup> See Chapter 67 for description of the equipment used in molding.

<sup>2</sup> A few highly specialized operations have not been included since they do not fit into the table readily. For example, the method best described as "plastering" or modeling, by which large tanks are finished with resinous compositions, has been omitted.

<sup>3</sup> H. L. Grant and W. R. Farren, U. S. P. 1,612,576, Dec. 28, 1926, to Atlas Powder Co.; *Chem. Abs.*, 1927, 21, 617.

<sup>4</sup> The details of this operation are given in Chapter 22.

<sup>5</sup> M. Helfreich, U. S. P. 1,668,590, May 8, 1928; *Chem. Abs.*, 1928, 22, 3282.

	Casting		Thermoplastic Molding	
	a. Non-reactive	b. Reactive	a. Hot Mold	b. Cold Mold
Temperature of Mold to Start	Cold or warm	Warm	Hot	Cold or warm
Method of Softening Plastic	Heat	Heat	Heat	Heat
Where Softened—Inside or Outside Mold	Outside	Outside	Outside	Outside
Method of Filling Mold	Gravity	Gravity	Pressure on mold	Pressure on mold
Method of Hardening	Cooling	Reaction	Pressure and cooling	Pressure and cooling
Temperature of Mold at End	Cold or warm	Cold or warm	Cold or warm	Cold or warm
Further Treatment	None	None	None	None
Relative Speed of Production	Slow	Slow	Fast	Fast
<i>Examples</i>				
Materials	Sulphur resin composition	Phenol-aldehyde resins	Vinyl resins, shellac	Asphalt-cumarone resin mixes
Typical Products	Seals	"Cast resin" products.	Phonograph records	Battery boxes

and around them. A permanent bond is said to be obtained without cloudiness or irregularity at the boundaries. A similar result may be achieved<sup>6</sup> by inserting a series of slightly separated nickel plates into the fluid mass of resin, which is hardened by heating, withdrawing the plates and filling the space with material of a different color. Sharply defined effects have been produced<sup>7</sup> by filling containers, such as tubes of cellulose acetate, with a colored liquid resin, immersing these in a mold in which they are surrounded by a similar material of contrasting appearance, and hardening the entire mass.

Weber<sup>8</sup> has made variegated rods of artificial horn or synthetic resins by placing irregular-surfaced layers of composition loosely in a mold and filling the interstices with a liquid or pasty binder. Deutsch and Thorn<sup>9</sup> used a mold, without a bottom, suspended in molten metal to allow easy removal of the finished article.

**Thermoplastic Molding.** The molding or modeling of plastic products softened by heat is a very old industry.<sup>10</sup> Asphalt and the natural resins (shellac, copals and rosin)<sup>11</sup> formed the basis of a well-developed art long before the invention of synthetic resins. Shellac molding technic is applicable to all fusible synthetic resin compositions and a description of it will serve to illustrate the general practice.

The molding of shellac compositions on a small scale requires only a cooling

<sup>6</sup> British P. 303,103, 1927, to Herold A.-G.; *Chem. Abs.*, 1929, 23, 4584.

<sup>7</sup> German P. 531,376, 1929, to Chem. Fabr. K. Albert G.m.b.H.; *Chem. Abs.*, 1931, 25, 5585.

<sup>8</sup> E. Weber, German P. 538,065, 1923; *Chem. Abs.*, 1932, 26, 1732.

<sup>9</sup> L. Deutsch and I. Thorn, German P. 412,189, 1923; *Kunststoffe*, 1925, 15, 124; *Chem. Abs.*, 1924, 18, 1555.

<sup>10</sup> See H. Abraham, "Asphalt and Allied Substances," 2nd Ed. D. Van Nostrand Co., New York, 1920. Chapter I. Asphaltic materials were molded or cast by the Sumerians about 3000 B.C.; statues and plaques made with asphalt are still preserved today. Glass, which is also handled as a thermoplastic, was cast in ancient times.

<sup>11</sup> For reviews of this subject see H. V. Potter, *J.S.C.I.*, 1933, 52 (May 19), 84. *British Plastics*, 1933, 4, 519. A. J. Gibson, *ibid.*, 1933, 4, 522. A. F. Suter, *ibid.*, 1930, 2, 77.

<i>Hot Molding</i>		<i>Extrusion Molding</i>		<i>Injection Molding</i>	
a. Without Cooling	b. With Cooling	a. Non-reactive	b. Reactive	a. Non-reactive	b. Reactive
Hot	Hot	Cold or warm	Hot	Cold or warm	Warm or hot
Heat	Heat	Heat and pressure	Heat and pressure	Heat and pressure	Heat and pressure
Either	Either	Outside	Outside	Outside	Outside
Pressure on mold	Pressure on mold	Pressure on plastic	Pressure on plastic	Pressure on plastic	Pressure on plastic
Pressure and reaction	Pressure and reaction	Pressure and cooling	Pressure and reaction	Pressure and cooling	Pressure and reaction
Hot	Warm or cold	Cold or warm	Hot	Cold or warm	Hot
None	None	None	None	None	None
Fast	Fast	Fast	Fast	Fast	Fast
Phenol- or urea-aldehyde	Phenol- or urea-aldehyde	Vinyl resins, Cellulose acetate	Phenol- or urea-aldehyde	Vinyl resins, Cellulose acetate	Phenol- or urea-aldehyde
Standard hot moldings	Precision and fine finish goods	Continuous moldings. Tubing.	Continuous moldings and sheets	Bottle and tube closures	Complicated parts

press and a hot plate heated by steam at 60-100 pounds pressure. The composition, made by thoroughly incorporating shellac (or synthetic resin) with fillers, is prepared in the form of sheets from which pieces are cut of appropriate size to fill each mold. These "blanks" are softened on the steam plate by the molder as he requires them, since such mixtures become brittle and worthless if heated for too long a period. The empty molds are heated in contact with the steam plate to the required temperature, about 80°C., filled with the softened blanks, and placed in the cooling press. The pressure applied, ranging from 700 to 2000 lbs. per sq. in., forces the softened composition to take the shape of the hot mold. After cooling in the press, the piece is removed and the cycle repeated. The finishing consists of removing the fin or flash, formed by the extrusion of material between the parts of the mold, and final polishing. Excessive temperature must be avoided during the entire operation, particularly in molding, inasmuch as it causes sticking, blistering and loss of finish.<sup>12</sup>

Another method of molding thermoplastic preparations is used to make large bulky objects such as storage battery boxes of asphalt or similar fusible materials. This method, in which the mold is not heated, is often called "cold molding,"<sup>13</sup> especially as it is now carried out in rubber factories where the hard rubber battery boxes replace those formerly produced.

Battery boxes are made of an asphaltic composition, usually containing gilsonite,

<sup>12</sup> Further examples of the molding of fusible or thermoplastic materials on a large scale in direct-heated molds are given in the section on Molding of Phonograph Records (p. 1334) which describes the use of shellac mixtures and the thermoplastic compositions containing vinyl resins or cellulose

4, 446.

<sup>13</sup> It has no connection with the cold-molding process of Chapter 66, in which the molded product requires baking to harden it.

a flux (a softer residual asphalt from oil refining or a low-melting cumarone resin), acid-resisting mineral fillers low in iron, some kind of fiber (asbestos, a long cotton flock or short cotton linters) and sometimes a small amount of new or



*Courtesy Modern Plastics*

FIG. 189.—An Abrasive Band Grinder or Sander Employed to Smooth Molded Synthetic Resins.

reclaimed rubber. The asphalts are melted and mixed with fillers and other ingredients in a kneader or masticator until homogeneous. The mass is divided into lots of 6-10 lbs. which are pressed, while hot and plastic, in collapsible water-

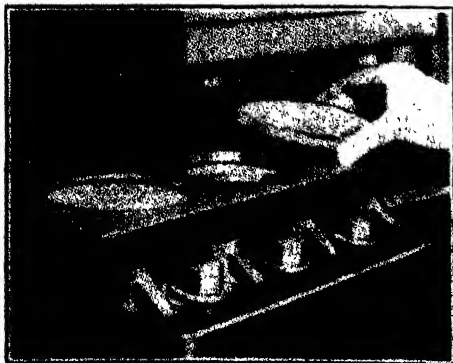


FIG. 190.

Molding with Preforms: Loading Tablets in Mold.

*Courtesy Bakelite Corporation*

cooled molds. Heating of the mold is unnecessary since the material flows into place before it has time to chill.

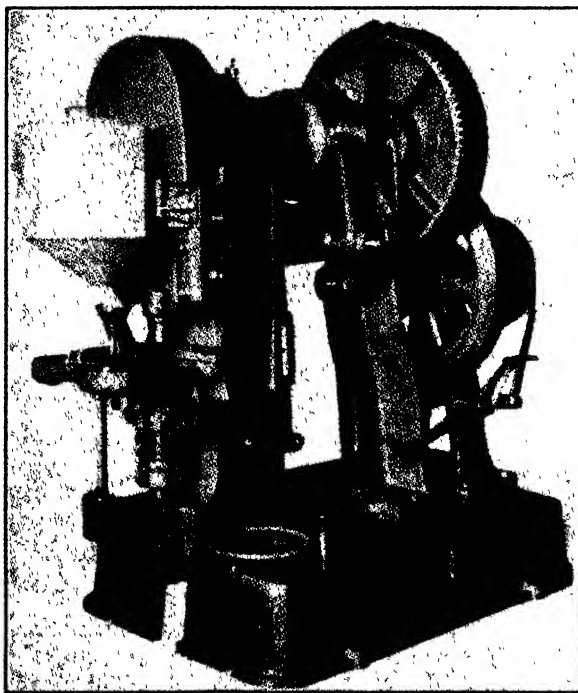
**Cold Molding.** The method widely known as "cold molding" consists of subjecting a special molding powder to very high impact pressure in a cold mold,

removing the piece at once, drying and baking without pressure under carefully controlled and gradually increasing temperatures.<sup>14</sup> The materials used are mostly the cheap asphalts and pitches with some shellac and cheaper natural resins, and sometimes include synthetic resins. High proportions of fillers are used (especially asbestos) and the mixture is fluxed with a small amount of solvent, sometimes a drying oil. In comparison with hot-molded products, those made by cold molding are usually cheaper, weaker and heavier, and have inferior surface finishes.

Certain refractory ceramic materials are molded by a very similar process, but they, of course, are burned at temperatures approximating 1000°C. These are also called "cold-molded" products, although they are sometimes distinguished as "cold-molded refractory" as compared to "cold-molded non-refractory."

#### PREFORMING OF MOLDING COMPOSITIONS

In hot-molding thermoreactive compositions, it has often been found convenient to convert the molding powders into the form of compressed masses variously



*Courtesy Arthur Colton Co.*

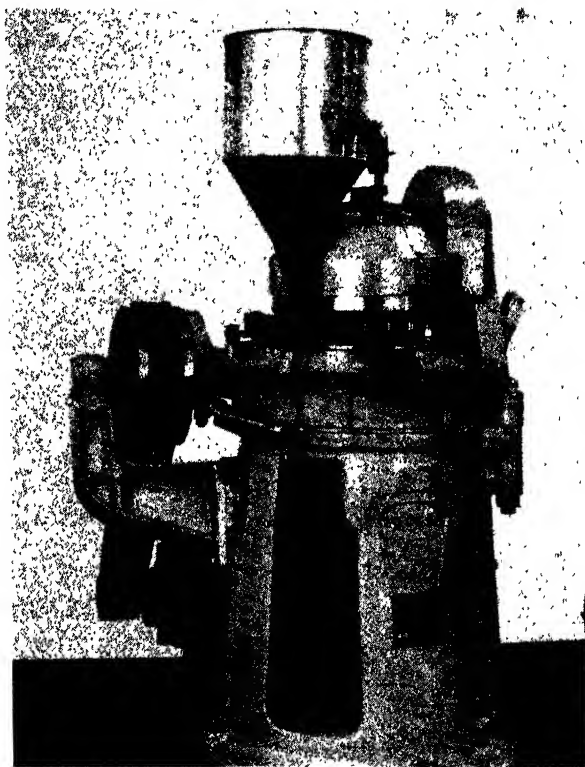
FIG. 191.—Single-Punch Preforming Press.

known as tablets, briquettes, pellets, pills, or preforms. (See Fig. 190.) They are made in machines similar to the pill machines which have been used in the pharmaceutical field for many years. Their production is really a molding operation and is properly considered in this separate section.

Tablets or preforms are made from the molding powder by applying high

<sup>14</sup> Details of composition, properties and manufacture are given in Chapter 86 together with descriptions of cold-molding presses.

pressure (five or six tons per sq. in.) quickly and without heat. The operation is very similar to the cold-molding process, except that no solvent is used and the treatment does not compress the material completely, but only causes the particles to cohere. The preform must be strong enough to be handled, and must soften and flow without crushing under the final hot-molding pressure. An average volume reduction is 50 per cent, so that a powder with an original bulk factor of  $2\frac{1}{2}$  would yield a preform of  $1\frac{1}{4}$  to  $1\frac{3}{8}$  which, of course, would be pressed to unit volume when all air is expelled in hot molding.<sup>15</sup>



*Courtesy F. J. Stokes Machine Co*

FIG. 192.—Rotary Preforming Press.

The shape of the preform may be made a close duplicate of the part to be molded, and the same general rules of mold design hold for preforms as for finished articles. One serious difficulty with preforms, however, is the making of deep narrow shapes. Nevertheless rectangular pieces with holes for inserts, pins or positioning rods, have been successfully made. The length and width of the preform should be slightly less than those of the finished article, and plenty of clearance should be allowed for holes. The thickness is then made sufficiently great to furnish the required amount of material for the final molding operation. Preforming molds should be smooth enough to prevent sticking but they need not be highly polished.

For larger pieces a number of preforms may be used, all alike or each made

<sup>15</sup> Methods of determining bulk factor are given in Chapter 69.

to fit in a particular place. One or more balls<sup>16</sup> are sometimes used because they can be charged more quickly than other shapes.

**Preforming Presses.** Preforms are now molded exclusively by mechanical presses, although at one time small hand-operated hydraulic presses, somewhat like those used in cold molding, were employed. These had the advantage of allowing metallic inserts to be molded into the preform. Inserts are now generally omitted, grooves or depressions being left to accommodate them.

Two kinds of preforming presses are now in extensive use. Single-punch models are used most frequently for special shapes, small runs and general work, and rotary machines for quantity production. (See Figs. 191 and 192.) The former has a capacity ranging from 40 strokes per minute, up to 80 or 90 with small pieces. The rotary model, because of the large number of punches and dies used, can turn out 300 to 700 pieces in the same time. Where production does not warrant the expense of a full set of punches and dies, the rotaries can be run with a lesser number by plugging up the unused openings, and the output can still be maintained at a rate several times faster than from a single-punch machine with the advantages of more accurate work, smoother operation and low die-cost.

In either case the loose molding composition is fed from a hopper into a measuring device which determines the weight of the preform by the volume of the loose powder. For successful operation, all machines, therefore, depend entirely upon the uniformity of its density. The pressure must be applied slowly in preforming especially when very fine material is used, so that the air originally entrapped between the grains will escape. Variable speed drives may be required on this account for maximum efficiency.

**Granulating of Fine Powders.** Rotary machines are also used for granulating particularly bulky molding powders to reduce their volume and to make preforming easier. They compress the powder in the regular way after which the tablets are broken up by a granulator and re-pressed.

#### MOLDING OF HEAT-CONVERTIBLE RESINS

In the molding of heat-convertible or reactive resins the fusible composition is placed in the open mold, which is closed and subjected to heat and pressure for a specified length of time, after which the piece is removed as a finished infusible mass of the desired shape. The charge may be used in any of three forms, powder, preformed tablets or sheets.

**Pressures.** The molding pressures required vary considerably but are high in comparison with those employed in the rubber and celluloid industries and lower than those used in cold molding or in preforming. About 1 ton per sq. in. is generally used on phenol-aldehyde compositions and 1-2.5 tons per sq. in. on urea-aldehyde preparations. Often the pressure applied is considerably in excess of that actually required for proper shaping of the material. Intensities which are substantially lower than 1 ton per sq. in. may produce a thick fin or flash which is objectionable, but excessive pressures will damage the mold.

**Temperature and Time Requirements.** The temperature and time required in the molding of thermoreactive materials are directly related, and, of course, depend on the composition. The working range is from 300-450°F. (about 150-230°C.) for phenol-aldehyde products, with most work done between 300-350°F. (150-180°C.). Blount<sup>17</sup> has stated that light-colored compositions, shock-resistant articles containing pieces of woven fabric, or moldings requiring flow of the

<sup>16</sup> H. M. Buckman, *Plastics and Molded Products*, 1931, 7, 679.

<sup>17</sup> C. W. Blount, *Plastics and Molded Products*, 1931, 7, 660.

material into deep or narrow parts may often be advantageously molded at even lower temperatures. The time required for cure or reaction is reduced with greater heat, but the total time of the cycle may be increased, and the yield of perfect pieces lowered since better control is required to prevent waste. For example, above 375°F. (190°C.) it is usually necessary to cool the mold somewhat before removing the pieces and so prevent blistering or pitting of the surface.

The most common method of heating is by saturated steam at 80-175 lbs. per sq. in. pressure (corresponding to about 325-375°F. theoretical temperature at sea level). At 350°F. (176°C., corresponding to 120 lbs. steam pressure) most phenol-aldehyde compositions can be cured and removed from the molds without special cooling. The time required for small pieces is from 1 to 8 minutes. Resorcinol-aldehyde resins in thin sheets, however, can be cured at higher temperatures (around 450°F.) in 5 to 10 seconds.<sup>18</sup>

With the light-colored urea-aldehyde molding powders the temperature may be advantageously maintained in the lower ranges, often as low as 270°F.<sup>19</sup> and usually not over 300°F. Rogers<sup>20</sup> has called attention to the necessity for proper cure in developing water-resistance. Pieces with thick sections should be cured at the lower temperatures to prevent case-hardening and those with inserts must be treated with special thoroughness. Parker<sup>21</sup> has stated that British practice is to cure urea-aldehyde compositions at 280-290°F. (140-145°C.), and phenol-aldehyde at 320-330°F. (165-170°C.). Information on time<sup>22</sup> required for cure is seldom quoted exactly, since it depends on many factors, and must be worked out in each case to insure best results.<sup>23</sup>

**Molding of Powders.** In practically all molding of thermoreactive materials the composition is charged into a hot mold. Inserts may be warm or hot when set in position, or they may be placed in the mold and allowed to heat before the composition is added, as this improves the flow of material around them and gives a better anchorage. Positioning rods, on the other hand, should be inserted as late as possible and should be cold, to prevent adhesion and to allow easy removal. They may be cooled in water before insertion. The required amount of powder is placed in the mold and tamped down.

In handling the composition in powdered form it is necessary, especially when using positive molds, to weigh each charge accurately. Limits must be set at 1/64 of an ounce if the articles are small. Less accurate weighing will serve when flash molds are employed.

**Molding of Sheet Material.** Sheet material is generally used in the preparation of shellac and similar thermoplastic compositions but only to a small extent with the various thermoreactive materials. The stock is placed on a steam-heated plate, which is usually covered with a cloth (or by other means of partially insulating it from the hot surface) and allowed to remain long enough to soften. Then it is cut to a slab of the desired size, placed in the mold by hand and pressed. Powdered or granular thermosetting compositions have always been considered superior to those in sheet form because they cure faster and, at the same time, eliminate the necessity for hot tables. Mottled or striated articles may be made by mixing coarse fragments of sheet stock of different colors before molding, controlling the result by varying the hardness or flowing characteristics of the

<sup>18</sup> See K. Brandenburger, *Kunststoffe*, 1935, 25, 8, 29; *Chem. Abs.*, 1935, 29, 2257.

<sup>19</sup> C. W. Blount, *Plastics and Molded Products*, 1931, 7, 660.

<sup>20</sup> J. L. Rogers, *Plastics and Molded Products*, 1931, 7, 664.

<sup>21</sup> H. C. Parker, *J.S.C.I.*, 1933, 52, (May 19), 818.

<sup>22</sup> The instruments for measuring and controlling time and temperature cycles are described in Chapter 67.

<sup>23</sup> Methods for the determination of time of cure are given in Chapter 69.



different colors. Flake material is commonly used in molding by injection and mottled effects similar to wood or marble may be produced.

**Molding with Tablets or Preforms.** The advantages of charging the mold with a tablet of preformed material are so numerous that this method is widely used for the majority of moldings of thermoreactive materials in the United States, and extensively in other countries. Preforms make possible the use of the lighter and longer-lived flash-type molds. Inasmuch as they are already compressed, full molding pressure can be applied at once, "breathing" of the mold is usually not necessary, and their good heat-conductivity allows them to soften and flow quickly. Products made from tablets, which may be preheated to shorten cure, have the additional advantage of thin fins and hence small waste. Often this overflow from the hot-pressing of tablets can be remolded since it does not receive either the heat or the pressure necessary for cure. The spongy mass obtained as overflow may be mixed with fresh material and reworked, although this is not generally done on high-class goods because the low price of new composition does not warrant the risk of reducing the quality due to the presence of partially reacted resin.

Tablets eliminate the labor, inconvenience and waste of material occasioned by the use of sheet stock which must be carefully preheated on a steam plate and painstakingly packed in the mold. They possess the good qualities of the powder for most purposes and, in addition, greatly increase the output of the molding press. It must be borne in mind, however, that the use of tablets involves additional costs for molds and the preparation of the tablets, and that they are impractical when only a relatively small number of articles is required unless a standard pill can be utilized. Some molders hold that they can secure a more uniform finish on their products by using powder instead of preforms, but in general the former is used for small orders, for complicated shapes, for certain pieces with inserts, and, of course, for compositions which cannot be preformed satisfactorily in high-speed machines.

**Molding Fixtures and Accessories.** Various accessories have been developed to aid the operator in loading and unloading the press. Special winders or "spiders" are sometimes used to open hand molds in addition to the arbor press that is usually available. Charging-frames are also employed, particularly for large, multiple-cavity molds. Most presses are single-acting, so that any method which will speed up the ejection of the finished articles and charging of the new material is valuable. Alpeter<sup>24</sup> and Lynn<sup>25</sup> have described a rack for removing forty-nine telephone mouthpieces at one time. All molded products do not lend themselves to such easy handling, but usually many cavities can be charged at once. (See Fig. 193.) Alpeter has also described a rack for placing the metal bushings which form the threads at the bottom of a telephone mouthpiece. This can be applied to most inserts that are not anchored to the mold.

A frame carrying individual hoppers for each cavity can be used to drop the proper amount of powder into all portions of a multiple mold simultaneously. Simultaneous charging of preforms may be effected in the same way. Ball-shaped preforms can be fed by gravity and, as mentioned by Buckman,<sup>26</sup> may be preheated while rolling. The treatment must be such that if, for any reason, production is retarded or halted temporarily, the material will not be overheated and ruined. Preheating may be effected by a conveyor which passes through a small oven, or separate electric ovens with screen-bottom trays may be installed for each press

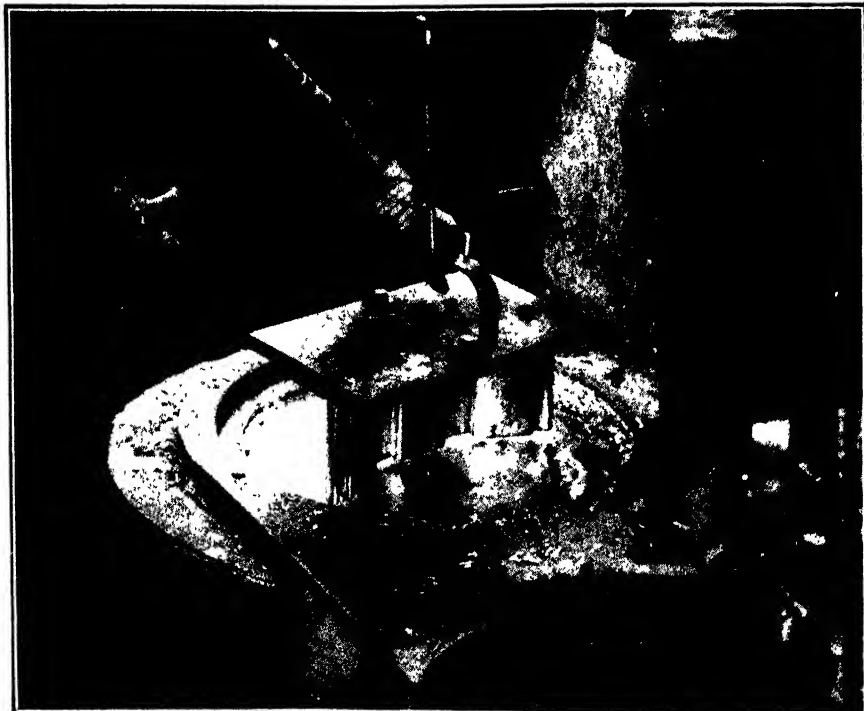
<sup>24</sup> W. G. Alpeter, *Plastics and Molded Products*, 1932, 8, 199.

<sup>25</sup> A. M. Lynn, *Plastics and Molded Products*, 1931, 7, 73.

<sup>26</sup> H. M. Buckman, *Plastics and Molded Products*, 1931, 7, 679.

or pair of presses, the preforms being left in just long enough to give the required degree of heating.

**Removal of Threaded Parts.** The removal of parts in which threads have been molded has always been a time-consuming operation. The difficulty may be partially solved by ejecting the bushing or plug containing the thread with the piece, loading a new metal part, and unscrewing the bushing or plug while outside of the mold. It has been suggested to remove bottle, jar and tube caps by



*Courtesy Catalin Corp.*

FIG. 193.—Making a Lead Mold.

springing them off over the threads of the mold without unscrewing, a practice which is occasionally possible due to higher elasticity of the material when hot. Shallow, rounded threads rather than sharp, square, or deep threads make this easier. Such methods of removal allow the inclusion of a retaining ring, molded on the inside of the cap to keep the cork liner in place.

#### EXTRUSION MOLDING

Extrusion and injection molding represent two points of view of the same action. If a plastic material is extruded from a receptacle in the form desired by applied pressure, then it can be said to be molded by extrusion. But if the composition is forced from this same container into a cavity which gives it the required shape, it has been molded by injection. Thus, although the two operations start out alike there is a real distinction between them. Forming of plastic materials by

extrusion is very old practice and has been used extensively in handling clay, soap, glass, celluloid, rubber and many other materials, in making pipe, tubing, tire treads, lead cable, brick, and carbon electrodes for arc lights.

This process has been applied to cellulose acetate and to vinyl resins. The extrusion of vinyl resin compositions in bars, tubes and moldings has been described by Davidson and McClure.<sup>27</sup> Leggat<sup>28</sup> has also reported apparatus and methods for forming rods or tubes of casein by this method.

Reactive resins have been extruded successfully, both in Germany and in England, according to Jones,<sup>29</sup> who prefers to call the operation *continuous molding*. The material in powdered or tablet form is fed into a hopper and forced by a ram through a molding zone. This consists first of a cooling portion where the powder is pressed into a compact mass of the desired cross-section, followed by a section where further heat and pressure are applied. It is thoroughly cured here and, after passing through a final stage designed to compress the material, emerges as a finished continuous molding. Many different shapes have been made by this method, including rods, tubes, beadings and special forms. Metal tubes can be coated on either the inside or outside, continuous sheets can be made, or perforated metal sheets covered. Extensive applications of extruded products in the building trades are forecast.

Extrusion was used by Eichengrün<sup>30</sup> to form a porous mass which was dried to a dry brittle powder suitable for molding. He has extruded a highly heated viscous solution of cellulose esters or ethers, which may contain synthetic resins or other materials, through a narrow orifice so that the issuing mass swells and the solvent evaporates.

The production of strips or bands from synthetic resins in a continuous apparatus has been described by Schless.<sup>31</sup>

#### INJECTION MOLDING OR PRESSURE CASTING

The injection or forcing of a plastic material into a closed mold is also referred to as the "squirting" process, transfer molding, or erroneously as extrusion molding. In many ways it is similar to the die-casting of metals.<sup>32</sup>

In all types of compression molds the pressure on the material is produced indirectly by the closing of the press, but the distinguishing feature of the injection method is that the mold is closed first and pressure is then applied to the material to force it into place. Thus it is possible to produce much more complicated moldings with thin walls because there is always a high positive pressure on the stock. This is held to be one of its chief advantages. Jenkins<sup>33</sup> has stated that the injection process applied to cellulose plastics gives products of higher tensile strength than compression methods because of an orientation of the chain molecules which occurs during the operation. Similar effects are recognized in rubber and in tough synthetic resins, such as certain vinyl polymerization products, where it is well known that the strength and other physical properties vary with the direction and amount of flow produced in the molding process.

<sup>27</sup> J. G. Davidson and H. B. McClure, *Ind. Eng. Chem.*, 1933, 25, 645; *Plastic Products*, 1933, 9, 143; *British Plastics*, 1933, 5, 14.

<sup>28</sup> A. Leggat, *British P.* 354,837, 1930, to Erinoid, Ltd.; *Chem. Abs.*, 1932, 27, 383.

<sup>29</sup> R. Jones, *British Plastics*, 1933, 4, 394.

<sup>30</sup> *British P.* 147,904, 1920, to Cellon-Werke Dr. A. Eichengrün; *Chem. Abs.*, 1921, 15, 173. *British P.* 290,939, 1927; *Chem. Abs.*, 1929, 23, 1267.

<sup>31</sup> S. Schless, *Austrian P.* 128,475, 1932; *Chem. Abs.*, 1932, 26, 4488.

<sup>32</sup> *British Plastics*, 1932, 4, 283.

<sup>33</sup> W. J. Jenkins, *J.S.C.I.*, 1933, 52, 245. Compare also work of Manfred and Obrist relating to the effects of mechanical working on physical properties of plastics: *Kolloid.-Z.*, 1927, 43, 41; *Chem. Abs.*, 1928, 22, 173.

**Injection Molding of Permanently Thermoplastic Material.** Buchholz<sup>34</sup> has described a method of injection molding of thermoplastic materials. The preparation is placed in a feeding-device where it is softened by heat and is forced into the mold through a constricted heated passage which tends to improve its flowing characteristics. The mold is maintained at a temperature below the solidifying point of the material which consequently hardens very quickly. The machine described by Buchholz is quite complicated, using a hand wheel, a hand lever, foot lever and several springs. However, much simpler injection mechanisms operated by one control are now available.<sup>35</sup> Larger models are power operated, most of them being of the horizontal type.<sup>36</sup> An air-operated machine has been used for regular injection molding, requiring pressures of from 600 to 900 pounds.

Stadlinger<sup>37</sup> has discussed the commercial injection molding of cellulose acetate and vinyl resins, describing particularly the early work on cellulose acetate molding powders for use in compression molds. According to Stadlinger, it was Eichengrün<sup>38</sup> who first recognized the possibilities of the injection molding<sup>39</sup> of cellulose acetate compositions and who suggested that they were best adapted to small articles weighing less than 10 grams. Temperatures of 130-170°C. (260-330°F.) with pressures of 450-900 lbs. per sq. in. have been recommended for such work.

Vinyl resins were molded by injection as early as 1929 by Posner.<sup>40</sup> More recent processes<sup>41</sup> have suggested injection molding of polymerized indene and styrene as well as vinyl esters. It has been maintained that thermoplastic compositions<sup>42</sup> were handled by similar methods in France as early as 1918 and that over 90 per cent of the bituminous-base battery boxes manufactured there in 1930 were formed in this manner.

**Injection Molding of Thermosetting Resins.** Since thermoreactive resins have been extruded, it has also proved possible to inject such compositions in the same way that thermoplastic compounds are handled with, of course, the additional step of hot curing. The cure may be carried out in the injection press, or the molds may be charged and transferred to another machine for further treatment. Thermoreactive powders were first molded by injection in 1930<sup>43</sup> and a special type of phenolic molding powder was described at that time<sup>44</sup> which was reported to eliminate "working" or polymerizing after treatment, as this composition was said to be incapable of reaching the "C" stage. No special equipment

<sup>34</sup> H. Buchholz, U. S. P. 1,810,126, June 16, 1931, to W. D. Grote; *Plastics and Molded Products*, 1932, 8, 18.

<sup>35</sup> See *British Plastics Year Book*, 1933, 105. Practical details of adjustment and operation of the machine are given.

<sup>36</sup> H. Chase, *Plastics and Molded Products*, 1932, 8, 239.

<sup>37</sup> H. Stadlinger, *Chem.-Ztg.*, 1932, 56, 409, 431; *Chem. Abs.*, 1932, 26, 4419; *British Plastics*, 1932, 3, 520. Injection of cellulose acetate compounds is also described, with further details, in *India Rubber J.*, 1931, 81, 11.

<sup>38</sup> A. Eichengrün and Hermann, German P. 393,873, 1919. A. Eichengrün, British P. 147,904, 1920. to Cellon-Werke Dr. A. Eichengrün; *Chem. Abs.*, 1921, 15, 173. German P. 395,083 and 395,084, 1919.

<sup>39</sup> German P. 441,023, 1919, to Lonarit G.m.b.H., since taken over by the Rhenisch-Westfälische Sprengstoff A.-G., now called the Dynamit A.-G. vorm. Alfred Nobel & Co., which at present owns all processes of the Cellon-Werke Dr. A. Eichengrün. See under Extrusion Molding, above. Cellulose acetate molding is done in England under the Eichengrün process (British P. 171,432, 1920, to Cellon-Werke Dr. A. Eichengrün; *Chem. Abs.*, 1921, 15, 173). For trade announcement see *British Plastics*, 1933, 4, 537. It was announced and publicly demonstrated there as early as February, 1930 (*British Plastics*, 1930, 1, 377, 438) and notice was served on unauthorized users in September of that year (*ibid.*, 1930, 2, 150, 161).

<sup>40</sup> F. Posner, German P. 540,552, 1929, to Deutsche Legrit G.m.b.H.; *Chem. Abs.*, 1932, 26, 2609. German Patent 557,686, 1931, addn. to 540,552, to I. G. Farbenind. A.-G.; *Chem. Abs.*, 1933, 27, 617.

<sup>41</sup> British P. 383,002, and 383,216, 1931, to I. G. Farbenind. A.-G.; *Brit Chem. Abs.* B, 1933, 79. E. E. Novotny (U. S. P. 1,997,074, April 9, 1935, to J. S. Stokes) uses very high pressures (60,000-100,000 pounds per square inch) in the charging chamber which supplies the cavities of the molds with plastic.

<sup>42</sup> *British Plastics*, 1930, 2, 296.

<sup>43</sup> *Ibid.*, 1930, 2, 66.

<sup>44</sup> *Ibid.*, 1930, 2, 52.

is required<sup>45</sup> as the injection cylinder and piston may be made as part of the mold. Chase,<sup>46</sup> and Hessen<sup>47</sup> have published further details of the operation.

Temperatures in this process range from 80-100°C. (170-212°F.) and pressures of 8500-14,000 lbs. per sq. in. fill the molds in approximately 15 seconds so that they may be removed and the cure completed in a hot press at about 1000 lbs. per sq. in. The time of cure is given as about 30-50 seconds per mm. (0.75-1.25 sec. per thousandth of an inch) of thickness at a mold temperature of 100°C. When the material is heated to the molding temperature as it is injected, Chase<sup>48</sup> found that thick parts cured more quickly than when compression molding is used. Special equipment<sup>49</sup> and special preparations<sup>50</sup> have been developed to meet various requirements.

Larger articles are now made by injection, especially where thin or complicated sections are called for, or where metal inserts are delicate and must be located exactly. These include twelve-cylinder automobile distributor covers<sup>51</sup> and manometer cases<sup>52</sup> over 15 inches long with molded threads at top and bottom.

Marble- and wood-effects are obtained by the injection molding of trays, smoking jars, ash trays and the like, using mixtures of several colors<sup>53</sup> introduced simultaneously through each of several inlets. For example, a tray 10 inches in diameter is made by employing three inlet ports in the base, located on a circle about five inches in diameter.

**Other Injection and Related Processes.** Synthetic resins have been used to impregnate containers molded of fibrous materials.<sup>54</sup> The resin is injected into a mold and heated until cured.

Kline<sup>55</sup> has stated that the interstices between the fibers in hot-molded products could be filled by forcing in a binder at pressures up to 500 pounds per sq. in. and temperatures of about 170°C., adding a solvent if necessary to secure penetration. The binder is subsequently cured by further heat. Gwaltney<sup>56</sup> has suggested that layers of sheet material could be cemented by a heat-hardened binder and the surfaces and outer layers of the sheets given a satin-like finish by using a hot pressure plate which had been plated with chromium.

Sauerbrey<sup>57</sup> has described a process for molding various materials by injection then subjecting the plastic mass to further pressure during hardening without further heating.

<sup>45</sup> *Ibid.*, 1930, 2, 296. An eighteen-cavity mold for tooth-brush handles is illustrated, and its operation with a cooperating cylinder and piston is described, charging three molds from the same plunger and piston, and finishing the cure in a separate press. All eighteen cavities are charged at once, each through two injection holes or inlets matching with outlets from the cylinder. Two or more holes are preferred to insure good mixing in the piece, and in general the more delicate the molding the smaller the inlet holes or nozzles should be. See also *ibid.*, 1933, 5, 71.

<sup>46</sup> H. Chase, *British Plastics*, 1933, 5, 29.

<sup>47</sup> R. Hessen, *British P.* 387,207, 1932, to A. Nowack A-G; *Brit. Chem. Abs.* B, 1933, 357.

<sup>48</sup> H. Chase, *British Plastics*, 1933, 5, 29.

<sup>49</sup> A double-acting hydraulic press is shown (*British Plastics*, 1931, 2, 574) and reference is made to direct-heated molds with flexible connections to allow a continuous cycle of injection, curing in a second press, cooling and stripping. Mold diameter should be about equal to the diameter of the injection ram. The most popular German machine (C. Stark, *British Plastics*, 1932, 4, 104) operates by air pressure reduced to 450 pounds from an initial pressure of 900 pounds per sq. in. A German mechanical press (Stark) uses a flywheel to generate the pressure for injection.

<sup>50</sup> "Ronisol" (phenol-formaldehyde) and "Ronilac" (urea-formaldehyde) molding compositions are used for injection molding in France (*British Plastics*, 1931, 2, 574; *Plastics and Molded Products*, 1932, 8, 239). They are available in three degrees of hardness, in all colors including white, for special purposes requiring high dielectric, mechanical, acid or heat resistance, and as odorless phenolic compositions for perfumery. The materials are usually softened at 100°C. and transferred to the injection cylinder at 60°C. (140°F.), at which temperature they will not cure even in an abnormally long time.

<sup>51</sup> For other developments in France, see *British Plastics*, 1931, 2, 574.

<sup>52</sup> *British Plastics*, 1931, 3, 243.

<sup>53</sup> *Ibid.*, 1931, 2, 396.

<sup>54</sup> French P. 707,101, 1930, to Soc. de Recherches & Brevets F. F. M. (Soc. Anon.); *Chem. Abs.*, 1932, 26, 559.

<sup>55</sup> H. Kline, *British P.* 347,738, 1929, to Bakelite Corp.; *Chem. Abs.*, 1933, 27, 382.

<sup>56</sup> A. E. Gwaltney, U. S. P. 1,991,090, Feb. 12, 1935, to Westinghouse Elec. & Mfg. Co.; *Chem. Abs.*, 1935, 29, 2264.

<sup>57</sup> W. Sauerbrey, *British P.* 357,992, 1930, to Jenalit Ges.; *Chem. Abs.*, 1933, 27, 385.

## PRACTICAL GENERAL MOLDING PROBLEMS

While various methods of molding have been described, there are a number of common difficulties that may be anticipated, typical of which is adhesion of the molded piece with subsequent breakage and difficulty of removal. Molding is an art, and experience is the best guide in meeting the many practical questions which arise. Each new mold and each new material may require some slight change in the method of handling. A few general rules can be given, however, with the hope that they will help to forestall the problems which may be expected.

**Sticking and Staining.** In the production of high-grade molded products difficulty may arise due to pieces sticking to the mold or due to the appearance of stains, discoloration or roughened areas on the finished articles. These two defects will be discussed together, since frequently in an attempt to overcome one problem, there will be a compensating trouble from the other. It is of utmost importance for best results to have a mold which is properly made, finished and polished. This should go without saying, but it is often responsible for a poor product. Next, and equally axiomatic, the mold must be clean and bright with a thin film of lubricant to prevent sticking. Scratches, roughness or dirt of any kind on the mold may be difficult to detect, and yet be sufficient to cause dirty pieces. For example, pencil marks on the mold are barely visible, but when a molding is made they are transferred to the piece and become very noticeable. On the other hand, the mold surfaces should not be chemically clean as this tends to cause adhesion. For best results a thin, continuous, invisible film of some lubricant, either applied separately as a "dope" or included in the composition itself, must be present. If this coating is removed, as by a solvent, sticking often occurs until it is replaced. However, too thick a film or one of the wrong kind will cause discoloration. This trouble may result from a number of causes, and may appear suddenly or gradually. Occasionally a stain will build up on the mold without showing on the piece until several have been molded. In the extreme case an oily smear may cover the whole piece so that it appears wet when removed from the mold.

**Chemical Sticking and Staining.** The question of chemical reaction between the metal of the mold and molding powder is important, especially in a new problem. Corrosion will prevent the formation of an adequate lubricating film, leading to serious sticking troubles, and, if severe, the mold may be etched beyond repair. Machine steel is the most common material but it cannot be used with thiourea-aldehyde resins or others containing large amounts of reactive sulphur as these compounds attack the hot mold, darkening and roughening it, thereby causing sticking and staining of the piece. The same result occurs when vinyl chloride resins are molded at high temperatures in copper or nickel molds, or when rubber containing sulphur is molded against copper, a combination actually used commercially to produce a permanent bond of rubber on metal.

Corrosion-resistant metals are required to meet special conditions.<sup>48</sup> Molds of stainless steel containing 14-18 per cent chromium are used to some extent, but these are expensive and more difficult to make than standard steel molds, and cannot be readily hardened. Chromium plating of molds for synthetic materials has been recommended and described at length by McKay.<sup>49</sup> Richardson<sup>50</sup> has recom-

<sup>48</sup> Metals suitable for use in molds are described in Chapter 67 from a mechanical standpoint.

<sup>49</sup> M. H. McKay, *Plastics and Molded Products*, 1931, 7, 552.

<sup>50</sup> F. E. Richardson, *Rubber Age*, 1928, 23, 607; *Chem. Abs.*, 1928, 22, 4272.

mended it for rubber and Mason<sup>61</sup> has referred to the successful use of this coating for both abrasion and corrosion resistance. The surface is, of course, very hard and smooth and can be used with most molding compositions, including those from thiourea, vinyl resins and rubber. Duralumin alloys<sup>62</sup> have also been used in molding hard rubber to prevent corrosion.

**Mechanical Sticking and Staining.** The degrees of sticking vary widely. Adhesion may cause only slight inconvenience in removing the piece, in no way damaging it or staining the mold, or separation may be almost impossible, resulting in a rough or a chipped piece or ruined form. Careful examination and study will often save much time in locating the cause of trouble. Repeated sticking or chipping in one place is often due to a slight defect in the mold, such as a scratch, dirt spot, or under-cut. In such cases the remedy is obvious.

Sticking and staining over larger areas, especially when there is variation in size or location, is usually caused by the composition or the method of molding. This indicates either that the necessary thin film of lubricant has not been built up, as in new or recently cleaned molds, that the film has been destroyed by excessive heat, or that the lubricant is unevenly distributed in the composition.

The use of too high a molding temperature will sometimes cause sticking and staining, as will also undercuring, or removing a thermoreactive composition before it has sufficiently hardened. Adhesion may also occur from too much cooling before stripping, especially of shellac and other compositions which are very brittle when cold. Rapid manipulation will usually help to overcome this trouble.

Thermosetting materials sometimes stick or show stains because pressure is applied at the wrong time or rate. If it is applied too rapidly staining is likely, whereas if the material is allowed to soften and then become infusible under heat without full pressure, staining accompanied by fine lines on the surface often occurs. This is the reason that fast-curing compounds cannot be used in making moldings requiring a protracted period of flow.

**Remedies for Sticking.** Since sticking is usually caused by the absence of a proper lubricating film between the mold and the molded piece, it can often be eliminated by a lubricant applied either directly or incorporated with the composition. The manufacturer of molding preparations always includes some agent of this type in his product, but the molder can easily add more if necessary. If sticking still persists, light machine oil, olive oil or common soap dissolved in water may be used to form a thin coating on the mold. Gasoline has been found helpful in the case of thermoplastic preparations made largely of shellac. Extremely small amounts must remain on the mold if staining or spotting is to be eliminated, however. A water-soluble sodium sulphonate compound obtained from mineral oil has been suggested to be useful as a mold lubricant<sup>63</sup> and certain solid lubricants (stearic acid, paraffin, ceresin and carnauba wax) have also been found to be of value. Dusting the mold with a finely powdered water-insoluble soap,<sup>64</sup> for example, zinc stearate or aluminum palmitate, has also been found efficacious. These compositions can be suspended in water by first wetting with alcohol to form a paste, and then diluting with water to form a solution to be used as a mold dope. Tallman<sup>65</sup> has applied aluminum stearate dispersed in a baked japan

<sup>61</sup> W. H. Mason, U. S. P. 1,844,861, Feb. 9, 1932, to Masonite Corp.; *Brit. Chem. Abs. B*, 1932, 1025; *British Plastics*, 1930, 1, 404.

<sup>62</sup> A. M. Lynn, *Plastics and Molded Products*, 1931, 7, 73.

<sup>63</sup> R. L. Sibley, U. S. P. 1,559,259, Oct. 27, 1925, to Standard Development Co.; *Chem. Abs.*, 1926, 20, 120.

<sup>64</sup> H. M. Weber, U. S. P. 1,558,440, Oct. 20, 1926, to Ellis-Foster Company; *Chem. Abs.*, 1926, 20, 513.

<sup>65</sup> A. P. Tallman, U. S. P. 1,682,213, Dec. 13, 1928.

to molds used for rubber. Edison<sup>66</sup> suggested gilsonite or other asphalt in a volatile solvent (naphtha) as a lubricant in similar work.

Manufacturers of molding compositions have studied this problem extensively and have overcome sticking to a great extent by the inclusion of film-forming lubricants in the material. Stearic acid particularly is utilized for this purpose. Huxham<sup>67</sup> suggested the incorporation of zinc stearate or aluminum palmitate directly in the preparation and this addition has been very helpful in preventing sticking of materials which would otherwise cause serious difficulty, for example, those containing a reactive phenol-furfural resin as a binder. The addition of water-insoluble soaps may be made to the resin or to the composition at any stage in its manufacture, or they may be precipitated on the filler. An effective method is to grind the metallic soap with the otherwise finished molding composition in such a manner that each particle becomes coated with the finely ground lubricant. The distribution must be uniform and an excess avoided.

Another material, recommended by Cherry and Kurath<sup>68</sup> for use in hot-molded articles, is the dark brown, waxy reaction product of stearic acid, aniline and either formaldehyde or furfural. A method suitable for large, rough-finished articles consists in coating the mold with a material which decomposes at the temperature used. For example, a resin-asbestos mixture may be cast in an iron mold lined with paper previously treated with acid sodium sulphate solution and dried.<sup>69</sup>

**Remedies for Staining.** Staining is by its very nature hard to overcome, because it is often caused by the presence of a substance incompatible with the resins under the conditions of operation. The manufacturer can control the ingredients but once a material is added it cannot be removed. The molder, therefore, must resort to dilution of the objectionable component by blending, that is the addition of other stock free from staining action. Thus, the operator who encounters staining can only dilute an unsatisfactory material, or change his pressing technic until the trouble is overcome or the material used up. Lower temperatures and longer cures should be tried, and the time of applying pressure should be varied. If the composition has been exposed to moisture, re-drying may be of value. A variety of operation adjustments should be considered as sometimes very small changes in manipulation are efficacious.

**Blistering.** Blisters in molded articles are produced by the expansion of gases or vapors formed or liberated during the molding operation. They may be small and distributed throughout the article or may unite into one or two large defects well below the surface. In any event, the appearance and strength of the product are seriously altered. With permanently fusible compositions, blisters are usually caused either by molding at too high a temperature or by opening the mold before it has been sufficiently cooled. If blistering continues after adjusting these two factors, the composition should be examined, since it may contain moisture or solvents used in its preparation, and further drying is needed to eliminate the difficulty.

When molding thermosetting or reactive phenolic resin compositions at a temperature not exceeding 350°F. (177°C.), blistering is not likely to be caused by improper treatment but is more often traceable to the presence of solvents or moisture. On the other hand, excessively high molding temperatures and subsequent opening of molds without any cooling may cause blistering. The use of a cooling press adds one more step to the procedure and should be unnecessary with

<sup>66</sup> T. A. Edison, U. S. P. 1,862,740, June 14, 1932, to T. A. Edison, Inc.

<sup>67</sup> T. S. Huxham, U. S. P. 1,571,447, Feb. 2, 1926, to Carleton Ellis; *Chem. Abs.*, 1926, 20, 997.

<sup>68</sup> O. A. Cherry and F. Kurath, U. S. P. 1,898,069, Feb. 7, 1933, to Economy Fuse & Mfg. Co.; *Chem. Abs.*, 1933, 27, 2841.

<sup>69</sup> German P. 528,447, 1929, to Säureschutz-Ges.m.b.H.; *Chem. Abs.*, 1931, 25, 4139.



thermosetting compositions when the platen temperature is maintained within the usual range. Pieces requiring accurate sizing are an exception, since they tend to warp and vary in dimensions unless cooled under pressure.

In molding thermoplastic goods, it sometimes happens that a blister, containing gas under high pressure, forms near the surface. When removed from the mold the gas pressure fractures the material and blows out a piece of stock, leaving a hole with a little pit at the bottom where the gas was compressed. Such blow-outs generally occur shortly after removal of the article, but small raised blisters may continue to appear for a number of hours or even days after pressing, making inspection very difficult.

If pressings are made from a composition in sheet form, there is danger of folding or trapping air in the stock. This is particularly common with very adhesive materials and may even be caused by air originally trapped in the stock during the initial mixing, sheeting or calendering operation.<sup>70</sup>

**Heat Marks. Undulated Surface.** A rippled or uneven surface on molded articles made from compositions which become infusible on heating is attributed by some observers to the evolution of gases which form pockets between the mold surface and the material which is being molded. These very slight undulations are readily visible when the article is examined by reflected light. Whatever may be their cause, it is generally understood among molders that chilling the mold before opening will usually remedy the fault. Furthermore, this defect is not considered a serious one and the purchaser is often willing to condone a slight unevenness of surface to avoid the extra expense because of time taken in chilling the article. The author has observed the formation of this undulating surface in molding compositions having binders of a number of different kinds, including phenol-formaldehyde, urea-formaldehyde, acetone-formaldehyde and numerous other condensation resins.

With thermoplastic materials, heat marks may be much more serious. In some cases where too high a temperature or too long a heating period has been used, the preparation may flow out of a flash mold to such a degree that contraction occurs, leaving low spots sometimes an inch or more long. Reduction in heat will usually overcome this, and if the stock is heated before being placed in the molds, the treatment often suffices to permit a reduction in the temperature of molding.

Local heating or cooling may be necessary in certain cases. Sherts<sup>71</sup> has used this method to eliminate heat marks in molding cellulose acetate or nitrate into such articles as toothbrush handles. At the temperatures necessary to get good cutting-off of the flash at the edges of the mold he found that heat marks occurred only on the flat surfaces, and accordingly constructed small cooling channels near these surfaces.

**Control of Flow and Flow Marks.** Most thermosetting preparations are now available in several grades of hardness or flowing characteristics to meet the demands of the different kinds of molding. In general, the hardest grade that will give sufficient flow should be used. If the material is not sufficiently plastic at the given temperature of molding used, flow marks may appear. These are periodic, light and dark, cirrus-like markings in the finished article at right angles to the direction of flow. The composition may not be hot enough to flow under the pressure applied or it may have lost its plasticity through reaction caused by heat alone. This occurs with thermosetting compositions when preforms are improperly heated. Sheet stock which has been allowed to react too long will often show seams where pieces of the material have welded together. Careful preheating and

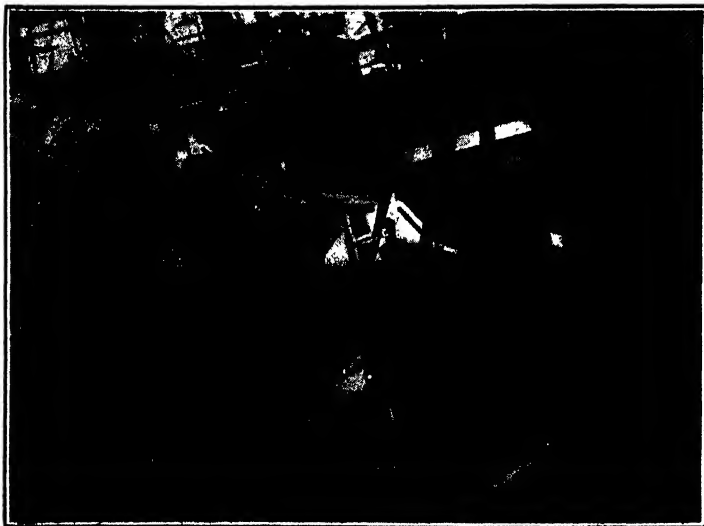
<sup>70</sup> Chapter 65 describes methods of eliminating air during mixing.

<sup>71</sup> J. H. Sherts, U. S. P. 1,819,444, Aug. 13, 1931, to Du Pont Viscoloid Co.; *Plastics and Molded Products*, 1932, 8, 114.

adjustment of the temperature and pressure in molding should eliminate this difficulty unless the composition is defective.

The flow of thermoplastic materials can be controlled by the temperature of molding and the timing. The stock temperature, the mold temperature, the time before cooling is started, and the final cooling temperature can all be varied. Tough preparations, such as cellulose acetate and certain vinyl resins, require a longer time to flow before cooling than do softer compositions having greater mobility at molding temperatures, such as shellac.

Flow marks of a different kind occur in the molding of transparent and translucent materials, especially where a filler or other substances capable of orientation are present. These defects are parallel to the direction of flow and are very diffi-



*Courtesy Bakelite Corp.*

FIG. 194.—Tumbling Barrels Remove the "Flash" or "Fins" Where the Mold Sections Come Together.

cult to eliminate entirely, but slower closing of the press or working at a higher temperature sometimes helps.

Waviness occasionally appears after stripping articles containing coarse fillers, such as long-fiber asbestos or rough fabric. The trouble may at times be caused by incomplete impregnation of the filler, and at others by strains around the particles. The grain of a paper will often show through a thin resin coating even when the fiber is thoroughly saturated. Exposure to water emphasizes these effects particularly when a non-waterproof filler is present.

**Finishing of Molded Articles.** The finishing and inspection room of the molding shop should be equipped with lathes, buffing wheels, polishing wheels and a variety of abrasives. Buffing wheels for this purpose are generally made of canvas or sheeting, sometimes treated with a sharp cutting abrasive for what is termed a "hard wheel." A very mild abrasive or grease alone gives a "soft wheel." A twelve-inch buff running at 1800 r.p.m. and having a surface speed of about 5700 feet per minute can be regarded as standard practice. Perhaps the most important task of the finishing room is the removal of fin or flash to leave as

little trace of these irregular projections on the molded article as possible. If the product is round it may be placed in a lathe and a file lightly applied to trim off the fin and leave a smooth surface, but light flash in an accessible position may be removed by buffing or by a sandpaper belt. In a few cases the operator must resort to filing by hand. This is usually necessary only with odd-shaped pieces but in general the practice in molding is to make the fin as thin as possible to minimize the labor in finishing. The fusible or shellac type of molded articles are polished on a soft wheel which is greased but has no abrasive. Here again if the product is round it may be possible to construct some sort of holder to allow lathe polishing. Infusible compositions are usually buffed on a hard wheel with tripoli, followed by polishing on a soft wheel which carries no abrasive. Inserts occasionally need to be machined after the article has been molded, an operation which is best done before buffing and polishing.

Finishing of small articles, including the removal of flash, is frequently satisfactorily accomplished by placing them in a tumbling barrel which rotates at slow speed and allows the pieces to rub against each other or against other objects placed there for that purpose. (See Fig. 194.) Considerable time is required, but a great many pieces may be treated simultaneously. Special polishing compounds are sometimes added in the tumbling barrel. Open-work tumblers are frequently used which allow the flash to fall through onto the floor as it is removed.

An "ashing" treatment used in finishing cast resins consists of wet-buffing with ashes or other soft abrasive and water. A "coloring" process used on some colored plastics (celluloid and cellulose acetate) applies lime and grease on a buffing wheel following tripoli or rouge.

**Inspection.** The inspection department is responsible for the quality of the product, and may make any tests necessary to insure this, varying from a casual observation as the goods are being packed for shipment to careful dimensional checks on every piece. Examination may be made of all articles, of hourly samples from each press or of representative specimens from the whole press room. The important points may be dimensions, location of inserts, waterproofness, flatness and freedom from small blemishes or polish of the surface. The list could be extended indefinitely. The final operations are packing and shipping.

**Costs and Cost Estimating.** The detailed methods of cost finding and cost estimating are obviously not within the scope of this book, but an appreciation of their importance and relation to the chemistry and chemical engineering of synthetic resins is most desirable. In fact, the question of expense is emphasized by Bender<sup>72</sup> as the point at which most new resins fail and the engineer on practical molding work is usually required to spend much of his time in attempts to reduce costs.

When a very few pieces are made the mold costs are high, although some companies are said to have found it profitable to build a complicated mold for as few as 200 impressions.<sup>73</sup> With hand molds and slow pressing cycles, labor costs are predominant. The development of semi- and fully-automatic machines has gone through the stage of excessive machine costs and now the material cost is one of the most important items as mechanical improvements have greatly increased the

<sup>72</sup> H. L. Bender, *Plastic Products*, 1933, 9, 106.

<sup>73</sup> Arrangements for loan, rental or exchange of molds have been proposed in attempts to distribute the mold costs among several users and prevent needless duplication. *Plastics and Molded Products* published in 1932 and 1933 (8, 422, 431, 459) give information on certain stock molds owned by various molders. Small orders of parts from these molds are accepted. A Central Bureau for molds has been established in Germany jointly by Siemens-Schuckertwerke A.-G. and H. Rommler A.-G., of Berlin-Spremburg. This is known as the Matrice Center, according to *British Plastics*, 1933, 4, 543, and has several thousand different molds available to the participating companies as required.

rate of production. This means that any saving made in the cost of raw materials is quickly reflected in that of finished articles.

An estimating sheet for the total cost of a molding has been prepared by Rowell<sup>74</sup> and methods of costing are discussed by Spall.<sup>75</sup> Quigley<sup>76</sup> considered mold costs with particular reference to the proper allocation of overhead charges, and has estimated the percentage of material lost from various causes in the average molding plant. The possible reuse of flash and ground rejects is of course an important item in this connection, and practice in this respect varies widely with local conditions in each plant.

#### SPECIAL METHODS AND PROCEDURES IN MOLDING

**Molding of Light-Colored Goods.** The demand for color in many of the articles of our everyday life has been met by the molding industry with an ever-increasing range, brilliance and permanence of colored compositions, especially in the lighter pastel shades. This has made it necessary to keep each color separate and free from contamination by darker preparations and any other discoloring agent. The molding industry has become, perforce, one of the clean trades, for even dust in the air can easily damage the lighter shades. All equipment used in preparing or handling the powders in any way, including preforming machines, must be capable of a quick, thorough cleaning, or, failing this, must be reserved for one color or one group of colors only. Urea-formaldehyde compositions require special care in preparation and handling because the market demands these in very delicate tints.

**Molding Radio Tube Bases.** This is a very specialized product made now by only a very few molding companies that have developed the necessary auxiliary equipment to make bases at the low price prevailing. Large, multiple-cavity molds are employed,<sup>77</sup> being loaded simultaneously with ball preforms. Hollow contact pins are commonly used, molded into the base in such a way as to leave an open hole through which the connecting wires may be passed.

**Forming Large Structures of Synthetic Resins.** Comparatively large moldings have been made with the regulation steel molds and presses. For example, bedsteads<sup>78</sup> (24 lbs.) have been formed in a mold (2½ tons) but because of the size and the large amount of material to be heated, the molding step is very slow, allowing the production of but four pieces per hour. A large tank,<sup>79</sup> 4 lbs. heavier than the bedstead, has been similarly press-molded. Radio cabinets 22 inches high, weighing about 10 pounds have been molded of phenol-formaldehyde composition in an eight-minute cycle.<sup>80</sup>

Acid-proof compositions of phenol-aldehyde resins and asbestos fillers (Haveg) have been developed to the point where large structures can be built for use in industry, providing chemically resistant tanks, agitators, pipes, trays, filter press plates and the like. Tanks up to 10 feet in diameter and 10 feet high can be made in one piece without seams. These are built up in forms from the resin-filler mixture in a condition much like cement or plaster, and are then hardened by means of heat. Methods of joining such sections to make large composite vessels have been described by Wirth,<sup>81</sup> who made acid-proof structures by cementing

<sup>74</sup> H. W. Rowell, *British Plastics*, 1931, 3, 94, 156.

<sup>75</sup> J. Spall, *ibid.*, 1932, 3, 342, 450.

<sup>76</sup> J. J. Quigley, *Plastics and Molded Products*, 1931, 7, 135.

<sup>77</sup> L. F. Rahm, *Plastics and Molded Products*, 1931, 7, 336.

<sup>78</sup> *British Plastics*, 1931, 3, 198. See also corrections, *ibid.*, 1932, 3, 396. The mold was made in a number of separate parts, hardened and then assembled.

<sup>79</sup> *British Plastics*, 1932, 3, 396. The mold weighed over 2½ tons.

<sup>80</sup> These were molded in a 850-ton press. Each half of the mold was built from one piece of steel, and then hardened.

<sup>81</sup> J. K. Wirth, U. S. P. 1,747,964, Feb. 18, 1930, and 1,789,642, Jan. 20, 1931.

together building elements with an adhesive or binder which hardens at room temperatures.<sup>82</sup> In Australia, plastic compositions have been used to make pipe<sup>83</sup> from 3 inches to 120 inches in diameter and up to 12 feet long for use as water mains and other general piping applications.

Large press moldings made from vinyl resin compositions have been described by Davidson and McClure.<sup>84</sup> These are panels 2 inches thick by 2½ feet wide and 8½ feet long, weighing 150 pounds. When used as wall sections they showed no tendency to warp or crack over a period of one year. Davidson and McClure have reported that a low degree of shrinkage occurs when vinyl resin is used and that, as compared particularly with curing resins, fewer strains are set up in the molded article. In one example which they have described, a layer of vinyl resin composition was molded over a porous sound-insulating and deadening core that had sufficient crushing resistance to withstand the molding pressure of 250 pounds per square inch. A very simple, makeshift mold was used, consisting of two aluminum plates and removable steel strips which formed a ring around the edges. The upper plate entered this ring about 0.5 inch when the mold was closed, thus forming a semi-positive mold. A layer of molding composition was spread evenly in the bottom of the mold, the core placed carefully in position with 0.5 inch clearance all around, and more molding composition added until the mold was fully charged. Steam was used to heat both the mold and the composition. Even with these crude conditions practically all of the panels formed were satisfactory for use.

**Methods of Ornamenting.** Variegated products have been made from plastic compositions by introducing flexible materials such as fabric, paper, leaves of trees, metal sheets with figured designs, wire or threads before the mass has set into final condition.<sup>85</sup> Lumps of synthetic resin have been covered with differently colored adhesives and molded to produce a veined effect.<sup>86</sup> Murphy and Owen<sup>87</sup> have decorated rubber or other materials, including synthetic resins, by coagulating emulsions or dispersions of rubber, gelatin or synthetic resins on their surfaces. The designs formed are irregular and may resemble leather. Dennis<sup>88</sup> has described the use of synthetic resins or casein for making molded ceiling roses or globes for electric lamps. Plates and other articles of synthetic resin are ornamented or modified by applying a mixture of a natural or synthetic resin and a filler with or without a pigment,<sup>89</sup> using pressure and heat to unite the powder layer with the surface of the article. Thompson<sup>90</sup> has treated rubber by imbedding globules (less than 1 mm. in diameter) of wholly or partly transparent material in its surface. Single<sup>91</sup> has also molded plastic articles bearing surface designs.

Decorative overlays, for example of cellulose acetate, may be applied to thermoplastic articles and welded in place by heat and pressure. These overlays should have lower plasticity than the base material.<sup>92</sup>

Urea-formaldehyde resin products have been embellished by Froese<sup>93</sup> to give

<sup>82</sup> J. K. Wirth, U. S. P. 1,867,060, July 19, 1932.

<sup>83</sup> *British Plastics*, 1933, 5, 25. The work was done by the Industrial Technical Research Institute, Sydney, Australia.

<sup>84</sup> J. G. Davidson and H. B. McClure, *Ind. Eng. Chem.*, 1933, 25, 645; *Plastic Products*, 1933, 9, 143; *British Plastics*, 1933, 5, facing p. 14.

<sup>85</sup> British P. 349,670, 1929, to N.-V. Philips' Gloeilampenfabriken; *Chem. Abs.*, 1933, 27, 436.

<sup>86</sup> British P. 349,753, 1929, to Synthaform Fabrik für Formteile aus Synthetischen Edelharzen Ges.; *Chem. Abs.*, 1933, 27, 435.

<sup>87</sup> E. A. Murphy and E. W. B. Owen, British P. 358,562, 1930, to Dunlop Rubber Co., Ltd. and Anode Rubber Co., Ltd.; *Chem. Abs.*, 1933, 27, 443.

<sup>88</sup> G. P. Dennis, British P. 330,133, 1929; *Chem. Abs.*, 1930, 24, 6042.

<sup>89</sup> E. Elbel, German P. 566,347, 1927, to Bakelite G.m.b.H.; *Chem. Abs.*, 1933, 27, 1221.

<sup>90</sup> F. Thompson, British P. 348,169, 1930; *Chem. Abs.*, 1933, 27, 631.

<sup>91</sup> O. Single, British P. 390,212, 1931, to Bakelite G.m.b.H.; *Brit. Chem. Abs. B*, 1933, 437.

<sup>92</sup> British P. 347,476, 1931, to Celluloid Corp.; *Brit. Chem. Abs. B*, 1931, 1107.

<sup>93</sup> E. Froese, U. S. P. 1,914,247, June 13, 1933.

a dark, sunken design surrounded by a lighter, raised border where the natural color has been bleached out of the resin composition. The result is accomplished by stamping or branding the surface for about four seconds with a metal die heated to a temperature ranging from 1000-1200°F. The brand should be shaped to fit the surface of the object. The burning or scorching forms the design in intaglio and at the same time darkens the material. At the edges the heat swells and bleaches the composition.

**Miscellaneous Procedures.** Mention should be made of water emulsions of synthetic resins, and their uses. Concentrations up to about 50 per cent of phenol-formaldehyde resins are available. These dispersions of resin in water have been used to make molding compositions, for example, with wood flour or sawdust. The filler is dampened with a dilute emulsion and the resin coagulated on the filler as the latter absorbs the water. Low-grade semi-porous moldings can be made from the dried filler with very much lower resin content than that in standard molding powders.

Emulsions may also be used in the preparation of sponge materials from resins by processes similar to those used in preparing sponge rubber from latex or artificial dispersions of rubber in water.<sup>94</sup> Porous sheets of rubber or synthetic resin compositions suitable for storage-battery separators have been made in this manner. A mechanical method for making these consists in piercing sheets of the uncured material with fine perforations and subsequently hardening by heat treatment.<sup>95</sup> Synthetic resin compositions containing a filler are used for connecting different parts of electric insulators.<sup>96</sup>

Hollow articles have been molded from synthetic resin powder by Ireland,<sup>97</sup> using fusible metal cores. Bray<sup>98</sup> has molded thin-walled sections, assembled these to form a hollow core, and introduced molding material to make a hollow article of which the core member forms a permanent part. Novotny<sup>99</sup> has suggested placing a potentially reactive resin mass around a core of a solidified gas, such as solid carbon dioxide, applying heat and pressure to gasify the core and cure the resin, producing a hollow article of the form desired.

Dillehay<sup>100</sup> modified the outside of bituminous composition moldings by rolling a charge of a plastic material (asphalt-filler mixture) in a molding powder containing a condensation resin to form a coating on the mass before molding.

A liquid mass of synthetic resin may be provided with resistance wires and the resin hardened by passing an electric current through the wires.<sup>101</sup> Hora<sup>102</sup> molded sliding-clasp fasteners for cloth in such a way as to allow attaching them to the fabric at the time of molding.

#### PHONOGRAPH RECORD MOLDING

The materials and methods used in the molding or pressing of phonograph records<sup>103</sup> show the changes which have been taking place in this industry. Some of

<sup>94</sup> G. W. Trowbridge, E. A. Murphy, D. F. Twiss and W. G. Gorham, *British P.* 333,952, 1929; *Brit. Chem. Abs. B.* 1930, 999.

<sup>95</sup> *British P.* 355,311, 1929, to Soc. Italiana Pirelli; *Chem. Abs.*, 1933, 27, 448.

<sup>96</sup> *British P.* 310,087, 1929, to Hermsdorf-Schönberg-Isolatoren Ges.; *Chem. Abs.*, 1930, 24, 672.

<sup>97</sup> W. F. Ireland, *British P.* 358,432, 1930, to Moulded Products, Ltd.; *Chem. Abs.*, 1933, 27, 455.

<sup>98</sup> G. R. R. Bray, *British P.* 364,741, 1930, to Brit. Thomson-Houston Co., Ltd.; *Chem. Abs.*, 1933, 27, 2052.

<sup>99</sup> E. E. Novotny, U. S. P. 1,776,368, Sept. 23, 1930, to J. S. Stokes.

<sup>100</sup> E. R. Dillehay, U. S. P. 1,891,918, Dec. 27, 1932, to Richardson Co.; *Chem. Abs.*, 1933, 27, 2080.

<sup>101</sup> E. Mohring, *French P.* 733,943, 1932, to Siureschutz-G.m.b.H.; *Chem. Abs.*, 1933, 27, 1221. *British P.* 360,326, 1932; *Brit. Chem. Abs. B.* 1933, 277.

<sup>102</sup> J. Hora, *British P.* 361,092, 1930; *Chem. Abs.*, 1933, 27, 1221.

<sup>103</sup> C. W. Rivise (*Plastics*, 1930, 6, 137, 155, 213, 277, 334, 397, 455) gave a review of 47 U. S.

the factors that have at last made synthetic resins competitors of the long-established shellac compositions will be indicated.

Phonograph records have been made from shellac since the early days of commercial production, when the compositions, then used for button manufacture and other moldings,<sup>104</sup> were found to make satisfactory records. So much shellac has been used by the record industry that for years this has been the controlling factor in its price. Many other materials, especially natural and synthetic resins, had been tried and used to some extent in records, but for the most part they were merely substitutes for shellac and did not contribute much to the art, either in quality of the record or quantity used. Since 1931 synthetic resins and cellulose derivatives,<sup>105</sup> including cellulose xanthate,<sup>106</sup> have been used for producing special records which are superior to shellac records in certain respects although they cost more to manufacture. Further extension is apparently largely dependent upon price and other commercial aspects rather than technical considerations.

The predominance of shellac in record manufacture for over thirty years is based on its peculiar advantages and on some other circumstances which will be mentioned briefly. Although far from perfect, it combines toughness, flow, and heat stability with hardness and sufficient water resistance to a greater degree than any other natural resin. The industry has developed methods which minimize its disadvantages, and which have been called "the high-water mark of molding technic."<sup>107</sup> Other materials with inferior molding qualities were not considered even if cheaper or better in some other way. The fact that shellac compositions could be reworked placed the curing resins at a disadvantageous price level which was further increased by the short molding time of the former. The large investment in stocks of shellac, necessitated by the time required for shipment from India, and in special equipment for handling, reduced the interest in any development which might jeopardize these investments. Furthermore, the acoustics of the old phonographs were so poor that they could not reproduce faithfully with the old records and would not give appreciably better results with the modern records. The introduction of the electric phonograph was the ruling cause of record improvement.

**Shellac Substitutes.** Repeated attempts have been made to use practically every plastic or resinous material for records, either alone or with shellac. All of the natural and fossil resins were tried without success except that small amounts have been used as plasticizers. Pitch from the destructive distillation of hardwood is used in cheap records, sometimes in considerable quantity, but gives rise to an inferior product. Permanently fusible acetaldehyde condensation resins have been tried but they cannot be used alone because of low melting point or lack of toughness. The same is true of fusible phenol-formaldehyde and alkyd resins. So-called nonbreakable records have been made to overcome the brittleness of shellac. For example, coal-tar pitch has been used as the chief impregnating material for paper pulp sheets which are united by heat and pressure into an unbreakable, though thermoplastic, record with a thin shellac composition surface. Thick records with a thin surface layer of phenol-formaldehyde resin<sup>108</sup> and a center

and 20 foreign patents relative to records. H. C. Bryson (*British Plastics*, 1929, 1, 187; 1930, 1, 326, 442, 484, 539) described general processes from recording to shipping. H. C. Bryson (*British Plastics*, 1931, 3, 104, 160, 223, 259) also discussed phonograph records in general, including new developments. In a later article (*J.S.C.I.*, 1932, 52, 495) he discussed various kinds of non-breakable records.

<sup>104</sup> A. F. Suter, *British Plastics*, 1930, 2, 77.

<sup>105</sup> W. T. Forre, F. W. Jones and G. Walters, U. S. P. 1,468,608 and 1,468,609, Sept. 18, 1923, to Columbia Gramophone Mfg. Co.

<sup>106</sup> H. C. Bryson, *British Plastics*, 1932, 4, 48, 90, 160, 206. J. E. Thornton, British P. 327,134 and 327,135, 1928; *Chem. Abs.*, 1930, 24, 5119.

<sup>107</sup> H. C. Bryson, *Chem. Age*, 1932, 27, 546.

<sup>108</sup> L. H. Bakeland, U. S. P. 1,053,264, Dec. 30, 1913, to General Bakelite Co. This covers a

layer about one-quarter of an inch thick made of paper or cardboard impregnated with a cheap mixture of resins have been marketed. This record was unbreakable, but it was heavy and bulky and had such a short life that it is not now manufactured. Gelatin records have been proposed, especially with the addition of softening and preserving agents.<sup>100</sup>

Shellac-surfaced laminated records have been made successfully. Here cheap natural resins and some pitches are used as a core, but the surface layer and thus the playing characteristics of the record are practically identical with those of solid shellac.

**Improvements by the Use of Synthetic Resins.** Synthetic resin records are much better acoustically, since they have less "background" or "surface noise" and reproduce much louder passages with fidelity. This is believed to result from their ability to yield finer grained, stronger compositions. The synthetic resin records have better wearing qualities, lighter weight and greater flexibility, and are less subject to breakage and to deterioration by moist air because of their superior water-resistance.

Cellulose acetate compositions have been used chiefly in manufacturing thin transparent records, and in laminated records with printing or illustrations in black and white, or even in four colors, under the acetate surface. Laminated records with colored, but necessarily opaque, shellac surfaces have also appeared.

**Production Methods.** The production of phonograph records, as previously mentioned, is a very specialized art, developed and operated for many years by the other record companies with shellac as the base material. The practice has so influenced the manufacture of all types that the fabrication of solid shellac records will first be described, followed by the modifications illustrating various steps in the introduction of synthetic resins into this field.

**Solid Shellac Records.** The raw materials for the usual solid or non-laminated shellac record are shellac, manila and other copals, rosin, cotton flock, carbon and bone black, nigrosine dye,<sup>101</sup> and mineral fillers. Hardwood pitch is added in the cheaper records.

The filler most frequently used is a red clay which is an iron aluminum silicate containing considerable free silica. Fine slate flour<sup>102</sup> of somewhat similar composition may be used. Some manufacturers prefer rotten stone (tripoli) with either ground barytes or blanc fixe, a mixture most often used for laminated records. The high specific gravity of the barytes makes a solid record containing it very heavy.

Shellac is the main component, to which smaller quantities of the other resins are added. Flock is usually about 3 per cent of the total weight. The blacks may vary from 2 per cent to 15 per cent, depending upon which ones are used and on the color of the mineral filler. The latter ranges from 45-75 per cent of the mix by weight, depending upon the kind used, the higher percentage, of course, applying to very heavy fillers. All components must be very fine and free from grit or coarse, hard particles.

The ingredients are ground separately, screened to remove foreign materials, and lumps, and then weighed out in the proportions required. Ground record scrap, made by breaking and grinding rejected records and press-room flash, is

non-thermoplastic sound record embodying an infusible condensation product of phenols and formaldehyde and includes both solid and laminated records.

<sup>100</sup> R. P. Rudin, *British P.* 890,543, 1931; *Brit. Chem. Abs. B*, 1933, 479.

<sup>101</sup> R. E. Sumner, U. S. P. 1,781,711, Nov. 18, 1930, to Calco Chemical Co.; *Chem. Abs.*, 1931, 25, 424. This refers to the use of ashine base dyes such as nigrosine base, or inulin base, and gives record composition formulas, showing the anticipated saving due to the use of dye.

<sup>102</sup> P. W. Stone, U. S. P. 1,623,293, Apr. 15, 1927, to Central Commercial Co.; *Chem. Abs.*, 1927, 21, 1693.



introduced at this point, and may constitute a considerable proportion of the mix. It is necessary to remove the paper labels from rejects before incorporation with the record composition. The dry powdered materials are thoroughly intermingled in the cold in a large mixer and small batches are weighed out for the grinding or milling operation. Either standard mill rolls or the larger enclosed Banbury mixers may be used.<sup>112</sup> The composition is ground for a short time at 100-105°C. (210-220°F.) until all lumps and unmixed material have been thoroughly dispersed. The hot plastic dough is now transferred as quickly as possible to "blanking" or calendaring rolls which form it into a long sheet while still hot. This sheet is marked into rectangles by rotating knives which cut it only part way through. When cold it is readily broken up into separate rectangular pieces, or "biscuits," each containing just enough material for one record.

**Pressing.** The type of press most used for solid records has a hinged, counter-balanced head. The cored steel flash-type dies are permanently attached, one section to the head of the press and the other below to the lower platen. The hydraulic ram is mounted in the body of the press and moves the lower platen and die upwards after the head of the press is lowered and locked in place. Each die contains a nickel-plated copper "matrix," made by electrolytic deposition on a wax blank containing the original recording.<sup>113</sup> The matrix is held in place by a ring which serves as the edge of the die and controls the thickness of the record. Matrices must be easily and quickly changed, especially when relatively few records of each kind are made.

The record molding operations were originally carried out by hand, but now, although the operations are the same, presses are used which are more or less automatic. The record molds are first heated by steam between 80-105°C. (175-220°F.), paper labels are placed in position on label pins, the hot soft stock from the steam table is placed in the center of the bottom matrix and the top of the press is closed and locked. The real pressing now starts as hydraulic pressure of about one ton per sq. in. of record surface is applied. The steam is turned off and cold water is passed through the same spiral channels in the mold blocks until the temperature drops to about 30-40°C. (85-105°F.). The hydraulic valve is then closed and the relief valve opened to drop the press. The head may now be raised and the record with its adhering flash removed. Cooling water is followed by steam, the relief valve closes, and the cycle is repeated. The operator removes the flash from each record while the next is in the press. Mechanical belt-driven toggle presses are used by some manufacturers, giving a pressure of about 1000 pounds per sq. in. The output varies with size and other conditions, but solid shellac records can be produced at a fair average rate of two per minute.

The records now go to the finishing lathe where the edges are smoothed and polished, either automatically or by hand. They are then wiped clean of dirt and dust, inspected visually and packed. Test records are played to detect any invisible defect.

**Laminated Records.** The laminated shellac record<sup>114</sup> has a thin surface layer of shellac composition coated on a paper disk which separates it from the cheap thermoplastic core. The surface material is similar to the solid record compositions except that it contains no flock. It is prepared in the same way, then ground to a fine powder and dusted onto the paper disks (slightly smaller than the finished record), which have previously been coated with a very heavy solution of shellac in alcohol. These are dried and pressed between hot rolls to com-

<sup>112</sup> See Chapter 65 for equipment and operation.

<sup>113</sup> B. A. Dimon, *Monthly Rev. Am. Electroplating Soc.*, 1932, 19, 7; *Chem. Abs.*, 1932, 26, 5501.

<sup>114</sup> H. C. Bryson, *J.S.C.I.*, 1933, 52, 495. R. Jones, *British Plastics*, 1932, 3, 357.

compact the material.<sup>115</sup> The core may contain coal-tar pitch, natural resins and sometimes a little linseed oil, together with cheap mineral fillers and usually some powdered mica to increase its strength. It is mixed and sheeted into biscuit as for solid records.

Pressing and finishing operations are very similar to those on solid records, except that a different type press may be used in which the two dies open like the covers of a book and are more accessible. The coated paper sheets or "spots" and the labels are placed in the press with the shellac sides toward the matrices. The softened core material is put in place between them just as for solid record pressing, and the same kind of a pressing cycle is used although a slightly longer cooling time is necessary because of the paper. Flash and rejected records, paper and all, are ground up and used again for the core.

Illustrated records with transparent surfaces may be made in the same way, except that a paper base and a transparent surface disk are used. Laminated records of this type have been proposed with cellulose acetate or nitrate surfaces on a cardboard instead of a plastic core, but have never come into extensive commercial use in the United States. Cellulose ester records with a cardboard base are more difficult to press than the plastic type, and rejected records are generally unfit for re-use.

**Vinyl Resin Records.** Vinyl resin records<sup>116</sup> made from the vinyl chloride resin with a small amount of vinyl acetate have had some commercial use in recent years. These are lighter, stronger and less brittle than shellac, and thus can be made much thinner. The finished record has low "scratch" or background noise and is less affected by the moisture of the air, because of the relatively better moisture-resistance of the resin and the absence of cotton flock, which is omitted as unnecessary because of the greater toughness of the resin itself. These advantages have allowed motion picture theatres to use twelve-inch vinyl resin records weighing four ounces each to replace the old standard sixteen-inch shellac records weighing twenty ounces. Shipping weight and breakage are both greatly reduced. Solid vinyl resin records have also replaced a laminated celluloid record with cardboard core, used for home recording. The new type not only avoids the possible fire hazard of celluloid, but appears to have better recording properties.

Vinyl resin compositions have a practical advantage in that they can be handled by the same equipment used for shellac with only minor changes in technique. Silica powder is used as a filler, in somewhat lower percentage than in shellac mixes. Fillers containing iron compounds cannot be used with vinyl chloride resins because of chemical reaction, although iron equipment causes no trouble. Mixing and pressing operations are conducted at slightly higher temperatures and are somewhat slower but otherwise they are similar to the procedure with shellac. Solid records are produced without cores, the resin remaining thermoplastic. Flash and rejects with label paper removed are worked back again into the mix just as with shellac, a very important factor in cost.

**Resorcinol Resin Records.** Records of heavy paper coated on one side with a resorcinol-formaldehyde resin composition<sup>117</sup> have also been used. They have always been made single faced because of the tendency of a double-coated sheet to blister during curing and the backs are waterproofed with lacquer to prevent

<sup>115</sup> W. T. Forre, U. S. P. 1,702,564, Feb. 19, 1929, to Columbia Phonograph Co.

<sup>116</sup> J. A. Davidson and H. B. McClure, *Ind. Eng. Chem.*, 1933, 25, 645; *Plastic Products*, 1933, 9, 143; *British Plastics*, 1933, 5, facing p. 14. This is a general article on applications of vinyl resins with many illustrations.

<sup>117</sup> H. T. Beans, *British P.* 237,976, 1929, to Durium Products Corp.; *Chem. Abs.*, 1931, 25, 2255; *British Plastics*, 1931, 3, 238. See also U. S. P. 1,915,282 and 1,915,384, June 27, 1933, to Durium Products Corp. Cf. also E. E. Novotny, U. S. P. 1,767,696, June 24, 1930, to J. S. Stokes. H. C. Bryson, *British Plastics*, 1931, 3, 233, 259.

curling. This record is lighter, thinner and less fragile than the standard shellac record.

The resin is formed in solution, a silica filler is added, and the thick, adhesive mixture is coated continuously on the paper as it comes from rolls. The resin coat is dried in a hot-air dryer and the coated paper is cut into large sheets which are allowed to season. Several records are pressed on a sheet at one time in a modified printing press with a gas-heated platen and a very short operating cycle. Subsequently, label information is printed on the surface, the back is sealed with lacquer, and the records are cut out of the sheet ready for inspection.

## Chapter 69

### Testing of Laminated and Molded Materials

Test methods and specifications are vital to those interested in the applications of synthetic resins because of the multiplicity of plastic materials proposed for identical purposes. In this situation, since competing products may be entirely dissimilar with respect to chemical composition or details of manufacture, bases of comparison have necessarily been drawn to reveal the properties in which the consumer is most interested. Thus, the established standards are found to cover such factors as tensile strength, elasticity, dielectric constant, hardness, resistance to abrasion and other characteristics having particular reference to the type of service expected from the finished article. Molders, manufacturers of resins and consumers of their products have from time to time developed their own specialized methods of test, but generally these have differed so widely from each other in point of view that they are of doubtful value as bases for uniform specifications.

However, all such procedures have been considered and given their proper weight in the development of the present standards of the industry. The National Bureau of Standards early recognized the need for investigation of the electrical properties of phenol-aldehyde resins and conducted several important researches on the subject.<sup>1</sup> Later, commercial laboratories became interested in the subject and developed methods for determining the physical and chemical properties of their products to supplement electrical tests. The American Society for Testing Materials undertook the task of unifying the results of various investigators in the field and its reports are now accepted by the industry in the United States. The methods of test given in this and the following chapter are based as far as possible on its recommendations.

In Germany, the methods of the Verein Deutsche Elektrizität and the Allgemeine Elektrizitäts-Gesellschaft differ in detail from American practice, while in France, standards have been approved by the Union des Syndicats de l'Electricité and by the French public services.

#### PART I

##### TESTS OF SHEET LAMINATED MATERIAL

The standard tests of laminated materials were originally developed to reveal their properties as electrical insulators, since this was formerly the most important application. However, they are equally useful in evaluating laminated sheets used for other purposes. The American Society for Testing Materials<sup>2</sup> has published a series of tentative standards and methods which form the basis of the tests here given.

**Tensile Strength.** The tensile strength can be determined on any available testing machine, using the standard tensile strength test specimen. (See Fig.

<sup>1</sup> H. L. Curtis, *Bur. Standards Sci. Papers*, 1914, 234; *J. Wash. Acad.*, 1914, 4, 492; *Chem. Abs.*, 1915, 9, 178. J. H. Dillinger and J. L. Preston, *Bur. Standards Technol. Paper*, 1922, 216; *Chem. Abs.*, 1923, 17, 319.

<sup>2</sup> A.S.T.M. *Tentative Standards (D229-32T)*, 1932, 871.

195.) Since the strength of laminated materials frequently varies according to the direction of the grain in the sheet it is essential that specimens be cut both with and across the sheet and that this direction be clearly designated in reporting results. The unit value for tensile strength is calculated from the force required to break the piece divided by the cross-sectional area, based upon the dimensions found before testing.

**Modulus of Elasticity.** It is sometimes desirable to determine the modulus of elasticity, that is, the stress required to produce a unit distortion. This can be readily done by means of an extensometer, measuring the elongation of a convenient gaged length at the middle portion of the test specimen under various definite loads.

$$\text{Young's Modulus of Elasticity} = E = \frac{\text{Stress}}{\text{Strain}} = \frac{FL}{Ae}$$

$F$  is the force applied in pounds.

$A$  is the area of the cross section of the test specimen in inches.

$L$  is the gage length in inches over which elongation is measured.

$e$  is the elongation of the gage length in inches.

**Flexural Strength.** In determining flexural strength, the specimen is tested as a simple beam loaded at the center. The contact edges of the supports on

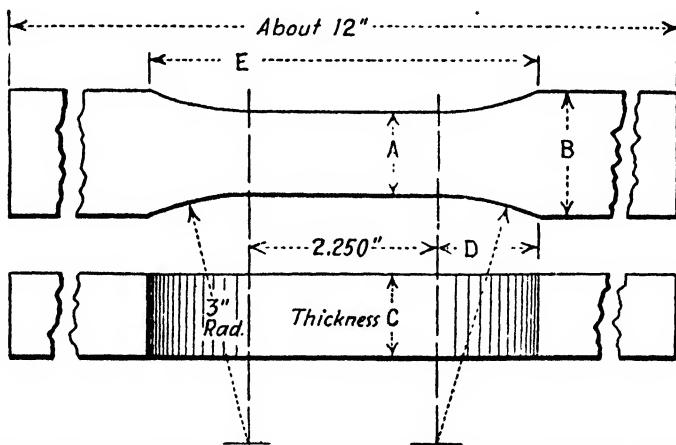


FIG. 195.—Tension Test Specimen for Laminated Sheet Insulating Materials.

which the specimen is placed are rounded to a radius of  $\frac{1}{8}$  inch for materials thicker than  $\frac{1}{8}$  inch, and to a radius of  $\frac{1}{16}$  inch for thinner materials. The distance between the points of support is 4 inches for edgewise tests of all thicknesses, and 8 times the nominal thickness of the material for tests in the flatwise direction, except that the minimum span is  $\frac{1}{2}$  inch. It is not recommended that tests be made in a flatwise direction for materials thinner than  $\frac{1}{32}$  inch, nor in an edgewise direction for materials thinner than  $\frac{1}{4}$  inch.

The specimen to be used flatwise is  $\frac{1}{2}$  inch in width unless the sheet is over  $\frac{1}{2}$  inch in thickness, in which case the width should be equal to the thickness. The latter dimension of the specimen is always the full thickness of the sheet from which the piece is cut. The length of the sample is 1 inch greater than the distance between the supports upon which it rests. As in the test for tensile

strength, specimens should be cut from the sheet both with and across the grain.

The maximum fiber stress in pounds per square inch is calculated from the flexural strength observations by the formula:

$$R = \frac{3PL}{2bd^2}$$

when:

*R* is the maximum fiber stress, or "Modulus of rupture" expressed in pounds per square inch.

*P* is the load in pounds.

*L* is the distance between the points of support in inches.

*b* is the width of the specimen in inches.

*d* is the thickness of the specimen in inches.

By observing the deflections of the specimen at the mid-point between the supports for different loads, the value of Young's modulus by bending can be calculated from the expression:

$$Y = 1/4 \frac{PL^3}{bd^3e}$$

when:

*Y* is Young's modulus for transverse loading.

*P* is the load on the bar at its mid-point in pounds producing the deflection of the mid-point *e* in inches.

*L*, *b*, and *d* have the same significance as in the expression for flexural strength.

**Compressive Strength.** In making tests for compressive strength a specimen in the form of a 1 inch cube is used for all materials which are 1 inch or greater in thickness. When it is desired to obtain the crushing strength of materials which are thinner than this, inch squares are cut and piled making a specimen at least 1 inch high. Materials thicker than 1 inch can be tested in either the flatwise or edgewise direction. However, sheets having thicknesses less than 1 inch are tested regularly in only one direction, that is, flatwise.

**Impact Strength.** The information to be obtained from the impact strength of materials is continually becoming of greater importance and has been reviewed by the American Society for Testing Materials.\* While these methods at the present time do not include tests on laminated materials, the same methods and apparatus can be readily used for such compositions, but a machine having a striking energy of 5 foot-pounds will be adequate for only the weakest laminated products. In order to cover the entire range of this class of materials 12-15 foot-pounds will be required. A specimen 0.5 inch by 0.5 inch by 2.5 inches will be satisfactory for the Izod test and one 0.5 inch by 0.5 inch by 5 inches for the Charpy test. (See Fig. 196.) The specimen may be notched or unnotched as desired, but care must be used in making comparisons between results obtained from the two types. It will be to advantage to confine control tests to one type of specimen. This is particularly true since the effect of the notch cannot be predicted with certainty. In determining the impact strength of laminated products the method will depend upon the thickness of the sample. Materials, either paper or cloth filled, having a thickness of  $\frac{1}{8}$  inch, may be tested either flatwise or edgewise. Specimens having a thickness of  $\frac{1}{8}$ - $\frac{1}{2}$  inch should be  $\frac{1}{2}$  inch wide, and of the same thickness as the original from which they are cut. The notch for laminated materials of  $\frac{1}{4}$  inch thickness or less, need only be 0.050 inch deep when the specimen is broken flatwise. When breaking edgewise, the standard notch of

\* A.S.T.M. Tentative Standards (D256-82T), 1933, 730.

0.100 inch should be used in all cases. In reporting the results the observer should specify the dimensions of the piece tested, the direction in which it was broken, whether it was notched or unnotched, and, if notched, the thickness back of the notch.

**Water-Absorption.** Since the absorption of water by laminated materials may have a very decided effect upon their mechanical and electrical properties, it is desirable to know something concerning their ability to resist such penetration.

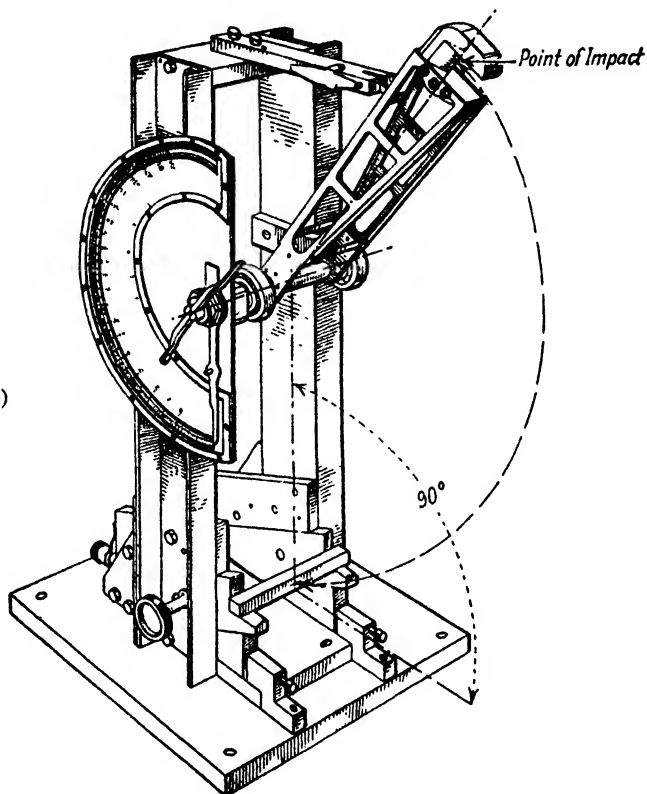


FIG 196.  
Simple Beam (Charpy)  
Impact Machine.

The measure of their water-absorption properties is usually determined by exposure to high-humidity atmospheres or by immersing the materials in water. Such conditions are more severe than are actually found in service, but they do represent the extremes of exposure. Although the absorption of water weakens the electrical characteristics of these materials, a certain amount of water may improve their mechanical properties. Eventually, however, these also are impaired by an excessive water content.

(a) *Rate of Absorption.* A suitable specimen for use with laminated materials is a rectangular strip of the same thickness as the sheet and 1 inch wide by 3 inches long. The edges of the piece should be carefully smoothed with fine sandpaper. Before immersing the specimen in water, it is weighed and then conditioned by drying for an hour at a temperature of  $105 \pm 1^\circ\text{C}$ . and afterwards placed in a desiccator at room temperature to cool after which the loss in weight

due to drying may be determined. The dried specimen is then immersed in distilled water at a temperature of  $25 \pm 2^\circ$  and, after 2 hours immersion it is removed from the water, wiped dry with a cloth and weighed. It is replaced and, after a total of 24 hours immersion, it is again removed, wiped and weighed. The percentage of water absorbed during both intervals is calculated on the basis of the weight of the dried specimen.

(b) *Total Absorption at Saturation.* If the sample is over  $\frac{1}{16}$  inch thick, materials of good quality will require an extremely long time to become saturated. Therefore the specimen for the saturation test should be machined and finished to  $\frac{1}{16}$  inch by 1 inch by 3 inches. It is dried as outlined above and immersed in distilled water. At intervals of 24 hours the piece is removed from the water and weighed. The weighings are repeated every 24 hours for the first week and then at intervals of 1 week thereafter until a difference of less than 1 per cent is found between successive weighings. The total water absorbed is, of course, the difference between this saturated weight and the original dried weight. The rate of absorption of water by laminated materials has been determined by many experimenters but only a few data have been published. Leopold and Johnston<sup>1</sup> have, however, reported results obtained on Bakelite strips 42, 71 and 139 mm. thick when immersed in distilled water. The work indicated that the specimen 139 mm. thick would not become saturated for a period of years. This only applies to resins and not to laminated or molded materials as the latter will reach saturation within the course of a few weeks if the recommended thicknesses are used.

(c) *Effect of Temperature on Water-Absorption.* In determining the water-absorption of laminated materials, it is essential that the temperature of the liquid in which the samples are immersed be maintained practically constant, since the permeability is greatly affected by temperature differences. The manner in which the absorption varies with the temperature may be found by testing at three different temperatures,  $25 \pm 1^\circ\text{C}$ .,  $50 \pm 1^\circ\text{C}$ ., and  $75 \pm 1^\circ\text{C}$ . This is best done by placing the vessel containing the water and specimens in a thermostatically controlled bath or oven. The rate of absorption (a) and the total absorption (b) can also be determined under these conditions.

(d) *Absorption in Humid Atmospheres.* Although laminated materials are seldom exposed to working conditions which involve total immersion, there are many cases when the material is subjected for considerable periods to high humidities. Hence, it is sometimes of interest to know something about the absorption of moisture at various humidities. The specimens are prepared as indicated and are weighed after they have been conditioned. They are then placed in warm atmospheres, say  $35^\circ\text{C}$ ., of varying moisture content, such as 75 per cent, 90 per cent and 0 per cent relative humidity, for various periods and the percentage of absorbed moisture is calculated. The exposure is continued at the respective humidities until successive weighings at 24-hour intervals do not differ by as much as 1 per cent of the total variation during the test. The 75 per cent relative humidity can be obtained by a sodium chloride solution having an excess of salt present. The 90 per cent relative humidity can be secured by the use of an aqueous supersaturated potassium nitrate solution. To obtain a dry atmosphere, it is best to use one of the aluminum salts or phosphorus pentoxide rather than sulphuric acid as the slight fumes will react upon the laminated material to a certain extent. The temperature of  $35^\circ\text{C}$ . is chosen as it is rarely exceeded in a laboratory during the warmest seasons.

(e) *Percentage of Volatile Material.* The specimen is prepared in accordance with the methods suggested for the determination of the rate of water-absorption.

<sup>1</sup> H. G. Leopold and J. Johnston, *J. Phys. Chem.*, 1928, 32, 876; *Chem. Abs.*, 1928, 22, 3080.



The sample is weighed as prepared and then dried in an oven at a temperature of  $110 \pm 1^\circ\text{C}$ . in an identical manner, but the drying is continued until successive weighings taken at 24-hour intervals show differences of less than 1 per cent of the total decrease in weight. Before weighing, the specimen should be cooled in a desiccator at room temperature. The difference between the original weight and the dried weight is the volatile content of the material. This volatile content may consist of both water and solvent remaining from the manufacturing process.

**Dielectric Strength.** The dielectric strength of laminated materials may be determined at commercial frequencies by a short-time test, a 1-minute step-by-step test or by an endurance test.<sup>a</sup> By any of the methods a 2-kilowatt transformer is required if 50,000 volts are to be used, and if greater potentials are to be employed a 5-kilowatt transformer is necessary.

The short-time test consists in raising the voltage continuously at the rate of 500 volts per second until breakdown occurs. The step-by-step test starts with a potential less than that required for breakdown and the voltage is increased in accordance with Table 69.

TABLE 69.—*Step-by-Step Test.*

Value Found for Breakdown by Short-Time Test	Initial Voltage	Increment of Increase
12.5 KV or less	2 KV	0.5 KV
12.5-25 KV	6 KV	1.0 KV
25-50 KV	12 KV	2.0 KV
50-100 KV	30 KV	5.0 KV
Over 100 KV	40 KV	10.0 KV

The voltage is held at each step 1 minute and the change to the next step is made within 10 seconds, the process continuing until breakdown occurs.

The endurance test is made at a temperature of  $100^\circ\text{C}$ . A voltage equal to 10 per cent of the maximum potential applied in the short time test is maintained for 30 minutes. The voltage is then increased by steps equal to 20 per cent of this initial value until puncture occurs. Each value is held for 30 minutes.

The endurance test subjects the material to the most severe conditions to be encountered in service. It is, however, of such a protracted nature that frequently too much time and expense are involved. On the other hand, the short-time test is entirely too mild and depends largely upon the rate at which the voltage is raised as well as the capacity of the testing outfit. It is quite difficult for different observers to obtain comparable results with manually controlled apparatus. The step-by-step procedure is therefore recommended as the most practical test since it is sufficiently severe to bring out the differences between materials. If it is desired, the effect of temperature may be taken into account.

It has been customary to make tests on built-up materials at right angles to the plane of laminations. For materials not over  $\frac{1}{4}$  inch thick, the test piece should be about 6 inches square and the electrodes should be 2 inches in diameter with edges rounded to a radius of  $\frac{1}{4}$  inch. Results are most satisfactory if the work is done under oil. When the dielectric strength is over 400 volts per mm., it will be necessary to have a transformer of more than 100,000 volts capacity for pieces a quarter of an inch thick. If potentials are greater than 100,000 volts, it may also be necessary to employ larger specimens even when tested under oil in order to prevent sparking over the edge.

Comparisons of dielectric strength should not be made between values obtained on specimens of different thicknesses, since the thinner the material tested, the

<sup>a</sup> *A.S.T.M. Tentative Standards (D149-38T)*, 1932, 814.

higher will be the dielectric strength per unit of thickness. Hence, in order to compare results obtained in different thicknesses, one should make appropriate corrections by means of a curve showing the variation of the dielectric strength

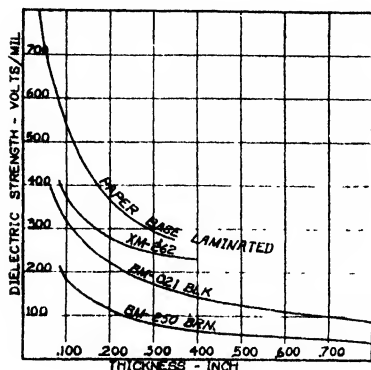


FIG. 197.

Variation of Dielectric Strength with Thickness of Test Piece. Step-by-step method was employed. BM-021 is a wood-flour-filled phenol resin molding composition. BM-250 and XM-262 are mineral-filled materials. (W. A. Zinzow and T. Hazen.)

*Courtesy Industrial and Engineering Chemistry*

with the thickness, and then all results should be reduced to a standard such as  $\frac{1}{8}$  inch. It is only by this procedure that one can obtain an approximate value for the breakdown of materials having greater thicknesses than can be punctured with the test equipment at hand.

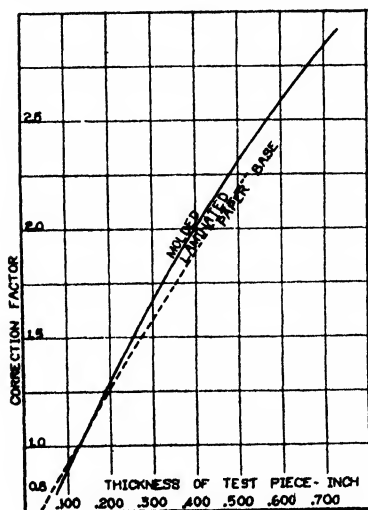


FIG. 198.

Correction Curve for Variation of Dielectric Strength with Thickness of Test Piece. (W. A. Zinzow and T. Hazen.)

*Courtesy Industrial and Engineering Chemistry*

This has been pointed out by Zinzow and Hazen.<sup>5a</sup> Figure 197 illustrates how the dielectric strength of some Bakelite materials varies with the thickness of the sample being tested. A correction curve for use when the pieces are not of standard thickness is shown in Fig. 198.

**Dielectric Strength Parallel to the Laminations.** It has been observed that laminated materials in service frequently break down along the laminations at voltages much lower than one would expect based upon the customary dielectric

<sup>5a</sup> W. A. Zinzow and T. Hazen, *Ind. Eng. Chem.*, 1935, 27, 899.

strength values. Such facts demonstrate that the dielectric strength along the laminations is quite different from that perpendicular to this plane. Hence, it is desirable to test such materials for breakdown along the laminations.

In determining the dielectric strength in this direction the test specimens are cut in squares 2 inches on a side and holes are drilled in opposite edges, at the mid-points, so as to line up perfectly, and to such a depth that the innermost ends of the holes will be exactly 0.5 inch apart. Metal electrodes are fitted snugly into the holes, thus forming a type of needle gap with the material between the ends of the electrodes. It is usually found convenient to make these holes of a diameter equal to one quarter the thickness of the material unless the specimen is extremely thin.

**Arcing Characteristics.** In devising a test for the arcing characteristics of synthetic compositions, it is essential that the procedure used be such as to give information bearing directly upon the particular application in question. If a material is to be subjected to an arc similar to that encountered in automobile ignition outfits, one type of test will differentiate the materials from each other. But if the product is to withstand actual burning under a strong arc, an entirely different method is essential.

For the former type of test, a 15,000 volt transformer is of ample size. The terminals may be placed about  $\frac{3}{4}$  inch apart on the surface of the material to be tested. The arc should be passed between the electrodes at regular intervals about 10 times per minute, each spark having a duration of approximately 0.1 second. This is continued until a carbon path is formed between the terminals. The urea and phthalic glyceride resins are particularly resistant to this form of test.

When dealing with power arcs, the filler is of importance, and it is necessary that it be one such as asbestos which resists actual burning. Numerous devices have been designed to test the power-arcing characteristics of various materials for very specialized applications, such as is the case when the arc is made by a brushing contact and is drawn out over the surface of the product. However, no single test which would give general satisfaction for all possible variations has as yet been proposed.

**Effect of Temperature on Dielectric Strength.** Since laminated material frequently becomes heated when in service, it is essential that something be known of the variation in dielectric strength with temperature changes. In general, a comparison of the strength at room temperature with that determined at 120°C. will be sufficient to predict the behavior of the material under warm working-conditions. If it is desired that the variation be shown by means of a curve, numerous points will have to be taken however. The elevated temperatures can be readily obtained by means of a thermostatically-controlled oil bath, but when making such tests sufficient time should be allowed so that the sample may come to constant heat before making the breakdown determinations. From 15 to 30 minutes will ordinarily be quite ample to establish this condition.

The effect of temperature on the dielectric strength of flat sheets and cylinders has been discussed by Flight.\* The temperature was varied from 30° to 100°C. on papers, mill products, varnished paper, cloth, fiber, wood and some molding compositions. The results showed that the decrease in dielectric strength varied from 15 per cent to 78 per cent at 100°C. as compared with the value obtained at 30°C. Flight suggested that insulating materials be tested at 100°C. and not at room temperature, or, even better, they should be tested at both temperatures.

\* W. S. Flight, *J. Inst. Elec. Engrs. (London)*, 1922, 60, 218; *J.S.C.I.*, 1922, 41, 222A.

Tables and graphs have been compiled by Nuttall<sup>7</sup> giving the relationship between decrease of breakdown and increase of temperature and the thickness of the material. He has determined values for hard rubber and many insulating materials, including Micarta and varnished paper.

**Effect of Frequency on Dielectric Strength.** Montsinger<sup>8</sup> studied the effect of time and frequency on the dielectric strength of various insulating materials and has compiled the relative dielectric strengths with varying frequencies. See Table 70.

TABLE 70.—*Variation of Dielectric Strength with Frequency.*

Frequency	Relative Dielectric Strength of Oil-Treated Pressboard	Relative Dielectric Strength of Solid Insulation
25 cycles.....	1 345	1.25
60 cycles.....	1 000	1.00
200 cycles.....	0.840	0.85
420 cycles.....	0.780	0.73

**Power Factor and Dielectric Constant.** A knowledge of the power factor of materials will aid greatly in classification. By this term, as applied to insulating materials, is meant the ratio of the power loss in a material to the product of the volts across a capacitor and the current in the same capacitor in which the material is used as a dielectric. The dielectric constant of the material is the ratio of the capacitance of a capacitor in which the material is used as a dielectric to the capacitance of the same capacitor with air as the dielectric. Another factor known as the loss factor is also of great help in classifying the various insulatory materials. The loss factor is frequently given as the product of power factor and the dielectric constant.

For flat plates the dielectric constant is readily calculated from the geometrical dimensions of the electrodes used, the thickness of the specimen and the capacitance as determined when making power factor measurements.

$$\text{Dielectric Constant} = K = \frac{(C - C_e)t}{0.0885A}$$

when:

$C$  is the capacitance in micro-microfarads as measured.

$C_e$  is the edge correction.<sup>9a</sup>

$t$  is the thickness of the specimen in cm.

$A$  is the area of each of the two equal electrodes in sq. cm.

0.0885 is a constant.

If the dimensions of the specimen are given in inches the above formula becomes

$$K = \frac{(C - C_e)t}{0.224A}$$

In case the specimen is in the form of a tube, the value of the dielectric constant may be calculated by the equation

$$\text{Dielectric Constant} = K = \frac{3.6t(C_1 - C_2)}{D(l_1 - l_2)}$$

when:

$t$  is the thickness of the tube in cm.

$D$  is the diameter (mean diam.) in cm.

$C_1$  is the measured capacitance of the tube in micro-microfarads for the electrodes of length  $l_1$ .

$C_2$  is the measured capacitance of the tube for electrodes of length  $l_2$ .

<sup>7</sup> W. H. Nuttall, *Trans. Inst. Rubber Ind.*, 1928, 4, 313; *Chem. Abs.*, 1929, 23, 1969.

<sup>8</sup> V. M. Montsinger, *Electrical World*, 1924, 84, 723; *Chem. Abs.*, 1924, 18, 3660.

<sup>9a</sup> Corrections given in A. S. T. M. *Tentative Standards*, 1932, 827.

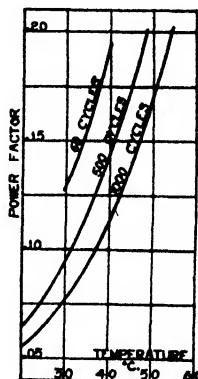
The American Society for Testing Materials, through its Committee D-9, has prepared methods for the determination of the power factor for 25-60 cycles or ordinary commercial power frequencies and for frequencies of the order of 1000 and 1,000,000 cycles.

Specimens for power-factor measurements can be prepared by taking pieces about 6 inches square and applying electrodes 4 inches in diameter. These contacts may be tinfoil secured by vaseline, or they may be painted using any suitable conducting paint. The electrodes are placed on each side of the sheet and directly opposite each other. Their size may have to be varied with different thicknesses in order that one will have a reasonable capacitance to measure.

Many factors may be brought to light by power-factor determinations. In practically all materials the presence of water will give a relatively high value at 60 and at 1000 cycles. While the addition of water also increases the losses at high frequencies, the change is much less marked than at low frequencies. After

FIG. 199.

Variation of Power Factor with Temperature. A standard wood-flour-filled phenol resin molding composition was used. (W. A. Zinzow and T. Hazen.)



Courtesy Industrial and Engineering Chemistry

baking, a piece of laminated phenolic stock will greatly improve with respect to power factor at both high and low frequencies. The heating produces further curing of the phenol resins with a resultant lowering of the losses, particularly at high frequencies. The baking also causes a drying action by driving off the water with the result that the losses are greatly decreased at the low frequencies.

Zinzow and Hazen<sup>10</sup> state that, if only one property of an insulator is to be tested, the power factor at low frequencies should be determined since it appears to be the best indicator of insulation qualities. Effect of frequency and temperature on the power factor of molded phenol-aldehyde resins is indicated in Fig. 199. Variation of power factor with moisture content is shown in Fig. 200.

Shearer<sup>9</sup> has shown that laminated phenolic materials have very little if any difference in their dielectric constant and power factor at 150 and 1500 kilocycles. This change in frequency is in the range where the variation to be expected in dielectric constant is relatively small. Tests at 60 cycles and 1000 kilocycles do show considerable differences depending upon the materials.

Dellinger and Preston<sup>10</sup> found some samples to exhibit changes in power factor with time and the season of the year. Following these observations, Preston and Hall<sup>11</sup> made a study of several representative samples, during 1920 and

<sup>10</sup> W. A. Zinzow and T. Hazen, *Ind. Eng. Chem.*, 1935, 27, 899.

<sup>9</sup> J. F. Shearer, *Phil. Mag.*, 1932, 15, 975; *Chem. Abs.*, 1932, 26, 3967.

<sup>10</sup> J. H. Dellinger and J. L. Preston, *Bur. Standards Technol. Paper*, 1922, 216; *Chem. Abs.*, 1923, 17, 819.

<sup>11</sup> J. L. Preston and E. L. Hall, *Bur. Standards Technol. Paper*, 1925, 284.

1921. From observations on about a dozen taken during the course of the year they drew the following conclusions: The power factor of the samples tested varied with the season of the year, reaching a maximum in late summer, usually lagging behind the seasonal variation of atmospheric humidity and temperature. In general, the power factor returned to its original value after undergoing a year's cyclic changes. A few of the samples showed a slight increase at the end of the year. The variation of power factor between two samples of the first grade of materials of the same make and color was greater than the amount of season variation. The seasonal variation for the second-grade materials was more than the difference between two samples of the material.

**Electrical Resistivity.** Inasmuch as both temperature and humidity have a most decided effect on the resistivity of laminated or molded material, it is highly desirable that the method of test adopted for the purpose can be applied under

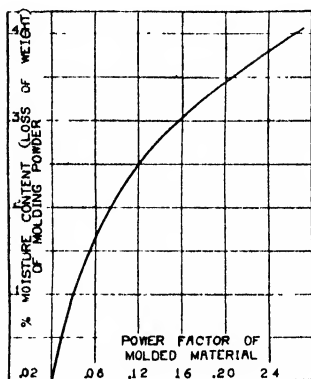


FIG. 200.

Variation of Power Factor of Molded Articles with Moisture Content of Molding Powder. Frequency 1000 Cycles (W. A. Zinzow and T. Hazen.)

*Courtesy Industrial and Engineering Chemistry*

special conditions. It is for this reason that the following procedure is suggested as more satisfactory than that proposed by the American Society\* for Testing Materials.<sup>12</sup>

The form of the specimen should be a rectangular strip 7½ inches long and 2½ inches wide. Spaced along the center line of the piece, at intervals of 1¼ inches, are bolts, ⅛ inch in diameter, fitted with washers ½ inch in diameter. Using the washers as terminals, it will be found convenient to measure the resistance of the intervening material under extreme conditions of moisture and temperature.

Exposure to humid conditions will cause a marked decrease in the resistance of most laminated materials. Exposure to elevated temperatures alone will cause the volume resistance to decrease enormously. Hence, determinations of this kind are extremely important in evaluating the relative qualities of different products. A material which has its surface resistance greatly affected by exposure to humid conditions or heat is certainly not as well suited for use where moisture or high temperatures may be encountered as one that is but slightly altered in the same length of time.

Owen and Thomas<sup>13</sup> have given a review of the available data on the application of synthetic resins to electrical insulating purposes. The materials were considered from the standpoint of their electrical and mechanical characteristics and

<sup>12</sup> A. S. T. M. Standards (D257-33), 1933, II, 1107.

<sup>13</sup> W. D. Owen and A. M. Thomas, *J. Oil, Colour Chem. Assoc.*, 1931, 14, 290; *Chem. Abs.*, 1932, 26, 609.

also in the light of their chemical structure. A special point brought out in the discussion was the fact that phenol-aldehyde materials manufactured with an alkaline catalyst differ considerably from those made in the presence of an acid catalyst.

**Hardness.** In general, determinations of hardness of laminated materials are not made by the same methods which are applied to metals. Certain of these tests have been of value in some cases, however, and the following methods have yielded good results.

(a) *Brinell Hardness.* This test consists in the determination of the amount of the indentation produced in the material by a load of 500 kg. applied to a ball 1 cm. in diameter placed on the surface of the material. The hardness is calculated as follows:

$$\text{Hardness} = H = \frac{P}{2\pi rd}$$

when:

$P$  is the force applied = 500 kg.

$r$  is the radius of the ball in millimeters = 50 mm.

$d$  is the depth of the indentation produced by the load on the ball and is read from a gage on the apparatus.

(b) *Scratch Hardness by Agate Point.* It is frequently of interest to have some measure of the relative ease with which various surfaces become marred or scratched during service. As yet no method has been adopted as standard; but a procedure, known as the agate-point scratch test, has been used quite satisfactorily as a means of distinguishing between the relative liability to scratching of various surfaced materials. A ground agate point in the form of a 90° cone is mounted in the end of a rod held perpendicular to the surface so that it may be drawn in this vertical position across the face of the sample. A collar is fastened on the rod bearing the agate point and various masses are added above this collar as desired. The weight is increased until the total mass bearing on the agate point is just sufficient to make the first visible scratch on the surface of the material. The scratch hardness is then stated as the total load required to produce this first marring. Such an apparatus is extremely simple but can be used quite advantageously in obtaining comparative results. A more elaborate piece of apparatus based upon this principle is so arranged that, as the scratching point is drawn over the surface in question, the total mass pressing down on the surface is gradually increased. The point at which the scratching point makes the first visible indentation on the surface is noted, and from this position the mass pressing on the point can be determined from the constants of the machine.<sup>14</sup>

**Coefficient of Friction.** Instances occur in which it is of interest to know something of the sliding resistance encountered when drawing a laminated product over the surface of some other material, but it is seldom that the static or rolling friction is of real importance. Consideration here shall be confined to the resistance offered when one material is moved over another surface, either of the same or different material.

A simple method of conducting the test consists of setting up a disc which can be rotated in such a manner that the material under test may be held against this revolving surface with various pressures. An arm concentric with the rotating disc may be employed to hold specimens at various distances from the axis of rotation and various masses can be applied to a weight holder. Such an arrangement permits the investigation of the effect of various surfaces, speeds and unit

<sup>14</sup> Certain of the hardness tests described in Chapter 70 for use with varnishes may also be employed.

pressures. The amount of the friction force is determined by pressing the end of the lever arm upon a suitable scale.

**Special Tests in Gear Stock.** In addition to the Charpy impact test, manufacturers of canvas-base materials have used other procedures to classify their products for use in gears. Of these, the following methods are typical.

(a) *Tooth Strength Test.* The simplest procedure for the determination of the endurance of gears is to allow a considerable mass to fall through a definite height, say 1 inch, so as to repeatedly strike one of the gear teeth on the pitch line. The weight is raised at regular intervals by means of a cam and lever arrangement and allowed to fall repeatedly until the tooth fails. The test can be repeated upon as many teeth as desired, so long as it is possible to hold the gear rigidly. In one arrangement every fourth tooth is destroyed. This test has a disadvantage in that it is necessary to prepare a finished gear and then test it to destruction without securing a real measure of its probable life in service.

(b) *Hammer Test on Gear Stock.* A method that has been found useful by some manufacturers of gear stock is made with the same apparatus as outlined above. However, instead of a finished gear a test section  $\frac{1}{4}$  inch by  $\frac{1}{4}$  inch by 1 inch cut from the gear stock is used. A mass of 25 lbs. is allowed to fall repeatedly from a 1-inch height so as to strike the test piece endwise until the piece is crushed. The specimen is cut in such a manner that it will be struck on the edge of the laminations.

(c) *Life Test on Gears.* The most satisfactory measure of the merits of a gear material is obtained by making life tests on products made from the material. The gear under test is used as an idler between a motor and a generator so that it can be subjected to various increasing loads and, in this way, run to destruction. While service under normal load gives the only true measure of the quality of a gear stock, it is not feasible to carry out all testing in this manner as it would require, under ordinary conditions, a prohibitive amount of time. The test can be accelerated by varying the load at stated intervals until the gear is destroyed as, for example, with the following routine which has been found to give a satisfactory index of endurance. A gear, which has been measured for thickness with a micrometer and similarly has been checked with a tooth comparator, is run at normal load for a period of 24 hours. The measurements are taken again subsequent to the initial run and the load is then increased to twice the normal figure, after which the gear is driven for a similar period. This process of increasing the driving force by increments equal to the normal load after each 24-hour run is continued until the gear fails. Employing a gear  $\frac{1}{2}$  inch thick, having forty-four  $14\frac{1}{2}^\circ$  spur teeth and a diameter of  $5\frac{1}{2}$  inches, it has been found that some materials fail under normal load, and some have lasted until the end of a 24-hour period at 4 times the rated or normal load. A tooth of the above-described gear will have a thickness at the pitch line of about 0.195 inch when new, but generally failure does not occur until the tooth has worn down to a thickness of 0.180-0.185 inch. For the poorer grades of material, however, the gears fail before the thickness of the teeth has been reduced to such a degree.

**Bonding Strength.** The extent to which the composite layers of a laminated product are bonded together is always of importance in classifying the type of material. This test is made on a specimen 1 inch square of the same thickness as the original sheet. Care should be taken in cutting so that the edges will be true and smooth. The piece is placed on edge and loads are applied to a steel ball, 1 cm. in diameter, which should be centered accurately between the two edges and the ends of the specimen. The load is increased until the sample splits. This



test is not readily applied to pieces which have a thickness less than  $\frac{1}{4}$  inch unless great care is taken, since the ball is likely to break out on one side, giving misleading results.

Another method which has been found to be quite satisfactory for a study of bonding strength, is to make use of the test specimen illustrated. (See Fig. 201.) The material to be tested can be cut into strips 1 inch wide and a hole,  $\frac{1}{8}$  inch in diameter, is then drilled parallel to the laminations at the exact mid-section. The sample is machined along the diameter of the hole and cut off so as to be exactly  $1\frac{1}{16}$  inch in length by 1 inch high when the piece is held with the groove on the top face. A drill rod  $\frac{1}{8}$  inch in diameter is placed in this channel and

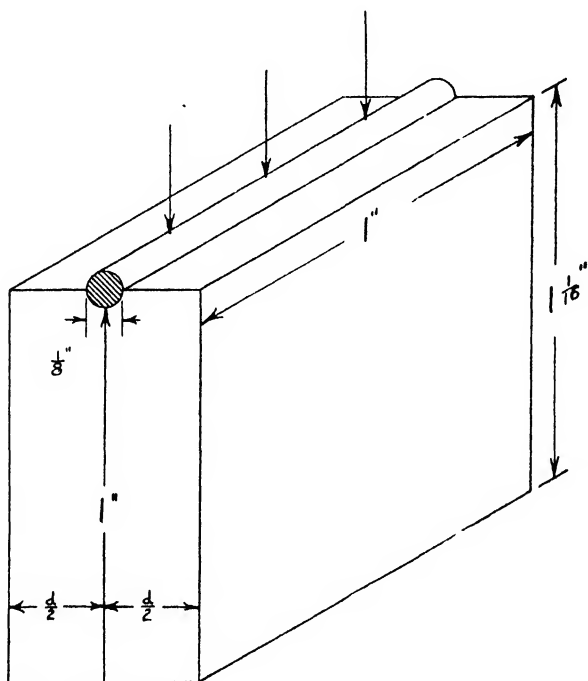


FIG. 201.—Specimen for the Determination of Bond Strength in Laminated Material.

pressure is applied on the drill rod until failure occurs. In testing materials less than  $\frac{1}{4}$  inch thick it is best to hold the specimen in a clamp that grips half-way up the piece so as to hold it firmly in a vertical position. If the sheet from which the samples are to be cut is extremely thin, a groove  $\frac{3}{64}$  inch in diameter may be used if the test piece is  $\frac{1}{2}$  inch square. Under these conditions a jig must of course be used to maintain rigidity.

**Cold Flow.** When laminated materials are so used in service that they are subjected to sustained pressures such as arise from tightening up bolts, distortion frequently occurs. This may be the result of either one or a combination of two causes; shrinkage may have taken place because of drying or else the material has distorted under the influence of a load which is greater than the elastic limit. Synthetic resin materials do not appear to have a sharply defined elastic limit as is true of steel and certain other metals since a load, small in proportion

to the maximum allowable fiber stress, will cause a permanent deformation which is not in accord with Hooke's law.

The specimen used in determining the cold flow of a laminated material is preferably a cube,  $\frac{1}{2}$  inch on a side, or, in the case of thin products,  $\frac{1}{2}$  inch squares piled up to give this form. The sample is subjected to a pressure of 1250 pounds, and the variation in height during the continued application of the load is determined by means of a micrometer gage at intervals over a period of 24 hours.

The Rockwell hardness machine may be adapted to determine the cold flow of these materials. A 100 kg. load is applied to a  $\frac{1}{8}$  inch diameter ball placed on the surface of the material. Measurements are made of the change in the depth of the indentation while the load is applied; and, if desired, these observations may be extended over several hours. It should be remembered that such tests are not well adapted to thin materials where the influence of the ball may extend through the specimen.

**Thermal Conductivity.** Determination of thermal conductivity of sheet materials is best made by the method which has been developed by the American Society for Testing Materials.<sup>16</sup> A sheet of material of known thermal characteristics is placed in series with the sheet of the material to be tested between surfaces one of which is at a higher temperature than the other. After equilibrium has been established in the flow of heat from the hot to the cold surface through the two materials, the drops in temperature through both the standard and the sample under test are determined by means of thermocouples placed at the mid-points of the sides of each specimen. A convenient size for the heating and cooling plates is 8 inches square if the samples are not over  $\frac{1}{2}$  inch thick.

The absolute thermal conductivity of a material requires a somewhat more elaborate procedure. Two specimens of the material to be tested are placed one on each side of a surface in which the heat is distributed uniformly. Such a source of heat is composed of two parts, a central heating surface of definite dimensions and a surrounding guard-ring heater so arranged that the temperature can be separately controlled. In the measurements, however, it is only necessary to determine the heat developed in the central heater. On the opposite sides of the specimen are two cooling surfaces, maintained at constant temperature by water-cooling. Thus the heat developed in the central heater flows laterally through the samples at right angles to the hot surfaces, and is absorbed by the cooling plates. The temperature drop in the specimen is measured by means of thermocouples.

**Distortion Under Heat.** When sheet material is placed in service it is subjected to variations both in fiber stress and in temperature. Since an increase in temperature decreases the allowable fiber stress, the relationships between distortion, unit stress, and temperature become of importance.

The following method<sup>16</sup> has been developed for use with molding materials, but it is equally applicable to laminated products. A test specimen 5 inches by  $\frac{1}{2}$  inch by  $\frac{1}{2}$  inch is placed on supports 4 inches apart and subjected to a load of 2.5 kg. at its mid-point. (See Fig. 202.) The temperature is raised at the rate of 1°C. every 2 minutes until the deflection at the center of the beam reaches 0.010 inch. The temperature at which this occurs is called the heat-distortion point for the material. While the method specifies the exact size of the specimen and the resultant distortion, these can be varied to suit individual requirements.

If the specimens are taken from sheets less than  $\frac{1}{2}$  inch thick the same pro-

<sup>16</sup> A.S.T.M. Tentative Standards (D352-51T), 1933, 795.

<sup>16</sup> A.S.T.M. Standards (D48-53), 1933, II, 1101.

cedure may be applied, provided the force used is reduced so that the same unit stress, 265 lbs. per square inch, is maintained in the test sample. If it is necessary to reduce the distance between supports, the critical distortion should be proportionately diminished.

**Deterioration Under Heat.** Indications of failure of laminated or molded products due to exposure to heat may be found within a reasonably short time if the material can be subjected to heating conditions which are more severe than those found in service.

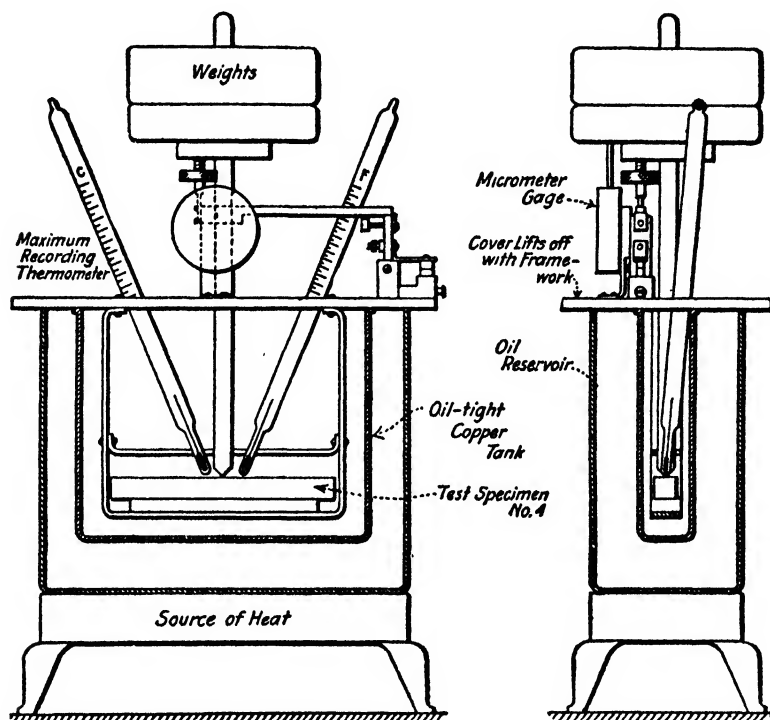


FIG. 202.—Apparatus for Temperature Tests.

The question generally arises as to what properties of the material will most readily show the ill effects of continued heating, since, in general, certain of the electrical coefficients tend to improve. However, it will be found that any of the mechanical properties are impaired by exposure to high temperatures. A specimen prepared for either impact, tension, crushing or transverse testing will fail at a lower point after subjection to heat for a considerable time. Accordingly, the procedure selected should be that which will measure the type of stress most likely to be encountered.

Having decided on the particular test, and therefore on the type of specimen, a large number of samples, usually about 100, are prepared and placed in an oven at approximately 150°C. Five or ten of the specimens should be tested prior to heating so as to obtain the values of the material before treatment is commenced. It is also necessary to previously determine whether or not the samples can be placed in an oven at such a temperature without causing them to blister.

To avoid this the samples can be exposed to a temperature of about 100-110°C., gradually raised to 150°C. during the course of 8-24 hours. The continuous heat treatment is then begun and tests may be made on groups of 5 specimens at intervals of 24 hours, 96 hours, 8 days, 16 days, and monthly thereafter. The specimens are first cooled to room temperature, upon removal from the oven, in a desiccator. They are then conditioned for 24 hours at 60 per cent relative humidity and 30°C. and finally tested under room conditions immediately after the conditioning. Such a series of tests will classify the materials as to their ability to withstand continuous service at elevated temperatures.

**Gloss.** The gloss or luster of a surface is usually reported as the reflecting power of the material. There are several instruments and methods that have been used for such determinations. These are, however, all designed for special applications. In the case of the Pfund glossmeter the material to be tested is rotated in such a way that light, falling upon this revolving surface, is reflected through a tube having a photometer at its end. Measurements are compared with the reflection from a glass surface as a standard and the results are given in relative terms. The Ries-Gilbert glossmeter employs a lamp as a source of light which, after reflection from the test surface, is measured by a photometer. The instrument can be so arranged as to indicate directly the light produced by the source. The values include not only the specular but the diffuse reflected light. Schulz<sup>17</sup> has compared the normal and diffuse reflection of light from a standard source by means of an instrument known as the Goerz "Glanzmesser." Polarization luster-measuring devices are somewhat inconvenient, however, as they require adjustment to the refractive index of the substance under examination.

## PART II

### TESTING OF MOLDING AND MOLDED MATERIALS

Certain of the test procedures<sup>18</sup> described in the preceding portion of this chapter may be applied to molded articles as well as to laminated materials. However, there is a group of examinations<sup>19</sup> developed for properties peculiar to molding compositions, and it is with these tests that this section will deal.

**Bulk Factor.** It is essential to know the bulk factor of a material if the molds in which it will be used are to be correctly designed. This characteristic is the ratio by volume of the loose molding powder to the resultant finished article. Knowing the maximum bulk factor of all materials to be used in a specific mold, the designer is able to calculate the cavity he must allow to hold a sufficient amount of powder. The usual method of determining this factor is to allow the molding powder to flow freely into a vessel of known volume. Then a piece, say a 2-inch disc, is molded, using the measured quantity of powder, and the volume of the molded piece is determined from its dimensions. The bulk factor may then be calculated from its definition.

Two other ratios are of importance in connection with molding powders. One of these is the ratio of the volume of the loose powder or molding composition to the resultant "pill" or preform when compressed in the customary way. The second ratio is that of the volume of the preform to that of the resultant molded piece. By preforming<sup>20</sup> the material, it is possible to use a mold having coincid-

<sup>17</sup> H. Schulz, *Textilber*, 1924, 5, 25; *Chem. Abs.*, 1924, 18, 934.

<sup>18</sup> The following tests, detailed for laminated materials, may be applied directly to molded articles without adaptation: Flexural strength, impact strength, water absorption, dielectric strength, arcing characteristics, power factor, dielectric constant, electrical resistivity, hardness, coefficient of friction, cold flow, thermal conductivity, deterioration due to heat, heat distortion, and gloss.

<sup>19</sup> A.S.T.M. Standards (D48-33), 1933, II, 1097.

<sup>20</sup> Reference should be made to Chapter 67 for a further discussion of preforming.

erable less volume than could be done were the powder used in the loose condition. In addition, this preliminary compression allows a better flow of the material during the molding operation. The possibility of entrapping gas within the finished article is minimized when using preforms.

**Density or Specific Gravity.** In the use of molding materials there are two densities that are of interest to manufacturers of finished articles. One of these is the specific gravity of the molded product and is of importance in determining the actual weight or mass of a finished piece. The other quantity is known as the density of the powder. It is necessary to know this value as well as the bulk factor in order to figure the cost of the material used in making a given product. This is due to the fact that the material is purchased by weight and that the quantity of material used by volume is determined from the bulk factor.

The density or specific gravity of the finished molded article can be determined by the usual method of weighing the piece in the air and again when suspended in liquid. For most molded materials water may be used, as absorption during the weighing operation is negligible.

The density of the molding powder may be obtained from the weight of a given volume of the powder. The material should be allowed to flow from a hopper into a container of known mass and capacity which may be subsequently weighed.

**Screen Analysis.** An analysis of the various screen sizes of the constituents of molding materials may be of considerable interest to both the manufacturer and consumer of molding materials. The consumer is particularly interested in a material of certain particle size such as will have definite characteristics during the molding operations. If the powder at one time has a high percentage of very coarse particles and a relatively small amount of fines, and later the distribution is reversed, considerable adjustment may be required to produce a satisfactory finished piece. A study of the size and distribution may be made by choosing a series of screens such as 8, 12, 16, 20, 34, 40, 50, 70, 100, and 140 mesh.<sup>21</sup> A weighed amount of the material is placed in the coarsest sieve at the top of the set when stacked as listed, and the whole assembly is agitated. The amount of material left on each screen will give an accurate estimation of the particle size and distribution when expressed as a percentage of the total mass employed.

**Tests for Molding Characteristics.** In connection with the development and use of new molding materials, it is necessary to make some tests to determine the manner in which the composition may be expected to mold under the conditions planned and also to determine what variations from standard procedures are desirable in order to give the most satisfactory product.

(a) *Cup-Closing-Time.* The cup-closing-time is probably the most widely used method designed to study the characteristics of a new material. Generally, the mold used will form a cup about  $2\frac{1}{2}$  inches high, having a diameter of 2 inches at the top and  $1\frac{3}{4}$  inches at the bottom, with a wall thickness of approximately 0.100 inch. The charge is placed in the mold, which should be at the temperature ordinarily used for that type of material. Pressure is applied and the time noted that is necessary for the composition to fuse, allowing the mold to completely close. If the cup fills out and has a good appearance, the test is considered satisfactory. If the piece is poorly formed or has a poor surface the tests will have to be repeated under various conditions of quantity of material, tem-

<sup>21</sup> These sizes have openings of 2380, 1630, 1190, 840, 590, 420, 297, 210, 149, and 105 microns respectively.

perature and pressure until a satisfactory cup is produced or it is shown that the material itself is at fault.

(b) *Disc Mold.* A test which has been of service consists of molding a thin disc, say  $\frac{1}{8}$  inch thick, and 4 or 5 inches in diameter. A material which will not flow to form a large-diameter disc from a small heap of powder will, in general, not prove to be useful for general commercial molding.

Another method which has been used to study the flowing characteristics of a molding preparation is to force the material through a measured orifice while in the fused state.<sup>23</sup> Several variations of this procedure have been found to be of value. In general, the methods are all similar in that they fuse the specimen powder in a cylindrical mold and then force it through an orifice of about  $\frac{1}{16}$  inch diameter. The time elapsing until the material ceases to flow through the opening has been suggested as an indication of the flowing characteristics. It is also possible to weigh the amount forced through the orifice and thus calculate the percentage of the total mass which was extruded.

The most intensive studies of plastic flow have all been based upon the ability of the material to pass through a small uniform or tapered opening. One such method has been described by Peakes<sup>24</sup> while Dillon and Johnston<sup>25</sup> have compiled data on the extrusion of rubber. They include in their article the theoretical and mathematical discussions of this and other test methods. Manfred and Obrist<sup>26</sup> have suggested that the plasticity of the molding composition bears a direct relationship to the physical characteristics such as modulus of elasticity and tensile strength of the finished product. Forrer<sup>27</sup> has reviewed the entire subject of the determination of the plasticity of molding compositions including the procedures for such examinations.

(c) *Setting-Time.* The setting-time of a material can be measured by the use of a cup mold, disc mold or by forcing the composition through a small orifice as described above. The setting-time must be considered for two different methods of treatment, however, since in some cases the material is cooled in the mold, while with other compositions it is removed hot. In either case this period is taken as the best interval in which one can obtain a satisfactorily molded piece.

**Tensile Strength.** The need of a standard tensile strength test was early realized by the American Society for Testing Materials, and their studies, extending over a number of years, have brought this phase of the examination of molding materials to a very satisfactory state.<sup>28</sup> Instead of the original specimen used for many years in connection with molding compositions and cement, a test shape has been developed which is so designed that the breaking strength is unaffected by the stresses due to the jaws holding the sample. (See Fig. 203.)

**Impact Strength.** A large proportion of the trouble caused by the breakage of molded materials in service can be attributed to their low impact strength. The most convenient tests on molded materials for their resistance to shock involves the use of the Izod (cantilever beam) or the Charpy (simple beam) machines.<sup>29</sup> This procedure is similar to that given for the testing of laminated materials, a notched specimen being used in both cases. Satisfactory results may be obtained with an unnotched sample, however, if care is taken, in fact impact tests have been made on pieces cut from finished articles.

Preferably, however, the specimens are  $\frac{1}{2}$  inch square in cross-section for both

<sup>23</sup> E. Karrer, *J. Rheology*, 1930, 1, 290; *Chem. Abs.*, 1930, 24, 5439.

<sup>24</sup> G. L. Peakes, *Plastic Products*, 1934, 10, 53.

<sup>25</sup> J. H. Dillon and M. Johnston, *Physics*, 1933, 4, 225; *Chem. Abs.*, 1933, 27, 4953.

<sup>26</sup> O. Manfred and J. Obrist, *Z. angew. Chem.*, 1928, 41, 971; *Chem. Abs.*, 1928, 22, 4674.

<sup>27</sup> M. Forrer, *Rev. gen. mat. plastiques*, 1932, 8, 259; *Chem. Abs.*, 1932, 26, 4821. Also *British Plastics*, 1932, 4, 19.

<sup>28</sup> A.S.T.M. Standards (D48-35), 1933, II, 1097.

<sup>29</sup> A.S.T.M. Tentative Standards (D396-35T), 1933, 730.

tests. The notch may be either milled or molded, but in any case should be cut at  $45^\circ$ , have a depth of 0.10 inch with its point rounded to a radius of 0.010 inch.

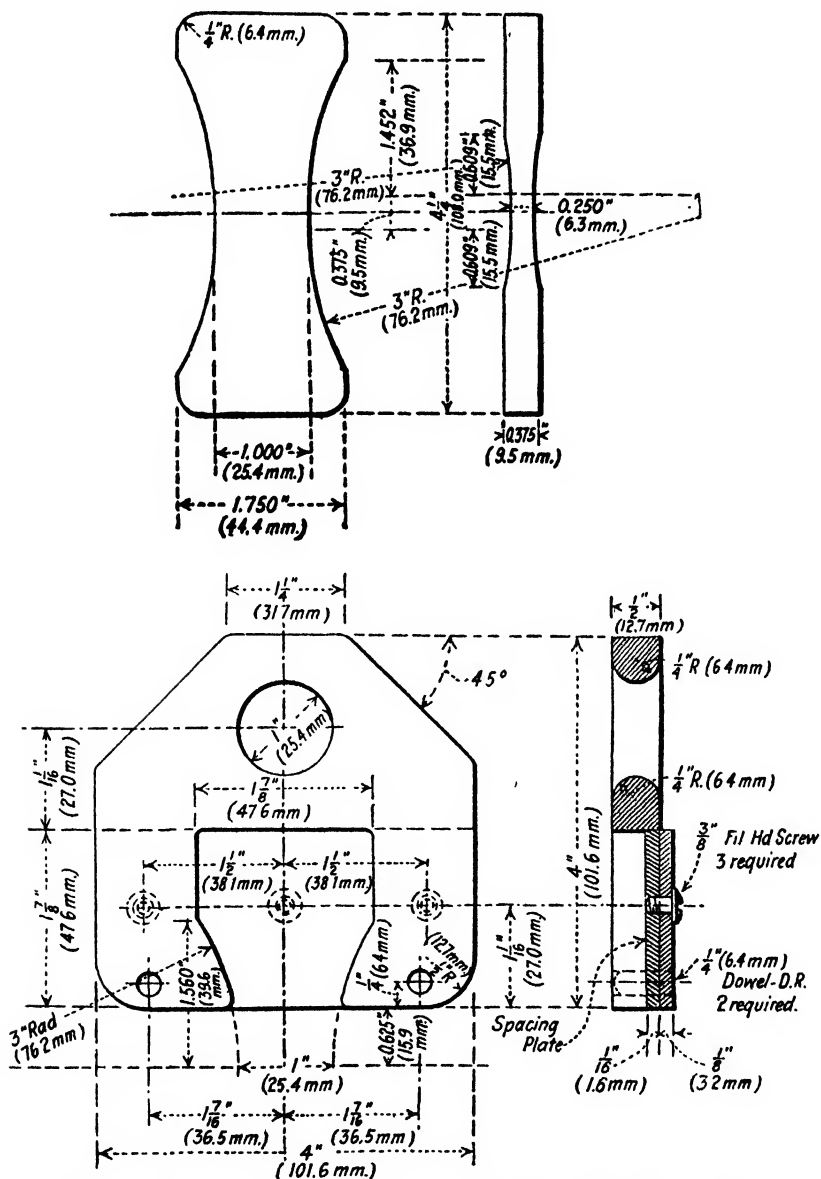


FIG. 203.—Tension Test Specimen and Holder for Molded Materials.

Although unnotched specimens may be used, it is desirable to check results given for such tests with those obtained with a notched sample from time to time since the discrepancy due to the lack of the notch varies with different materials.

In making the tests, the material should always be broken in the direction in which pressure was applied during the molding operation. Before making a test the specimens should be conditioned by placing them in an oven for 48 hours at a temperature of  $122 \pm 2^\circ\text{C}$ . The pieces may then be removed from the oven and cooled in a desiccator at room temperature before being tested.

**Compression Strength.** The standard specimen for compression testing of molding compounds is a cylinder  $1\frac{1}{8}$  inches in diameter and  $1\frac{1}{4}$  inches long.<sup>29</sup> The piece is molded in the direction of the axis of the cylinder. For control tests giving comparative results it may be quite satisfactory to make tests on other shaped specimens, however. Cubes,  $\frac{1}{2}$  inch on a side, have been used with very uniform results. Such shapes are well suited to determinations of the crushing strength in directions other than that in which the molding pressure was applied. It is of importance to exactly define the type of specimen employed in reporting the results of compression tests, as exact agreement can not be expected between samples of different shapes.

**Dielectric Strength of Molded Materials.** The general procedure is the same as that given under the corresponding test for laminated materials. The specimens used are discs of 4 inch diameter,  $\frac{1}{8}$  inch thick for hot-molded materials, and  $\frac{1}{4}$  inch thick if worked cold. The electrodes are also circular in form with a diameter of 1 inch. The test should be conducted under oil to avoid possible flashing over the surface. The procedure<sup>30</sup> may be either the short-time, step-by-step, or endurance variation as previously described, the sole difference being that in the short-time test the potential should be raised at the rate of 1000 instead of 500 volts per second.

<sup>29</sup> A.S.T.M. Standards (D48-35), 1933, II, 1099

<sup>30</sup> A.S.T.M. Standards (D48-35), 1933, II, 1102. See also E. A. Bevan, N. Strafford and E. E. Walker, *Trans. Inst. Rubber Industry*, 1931, 6, 384; *Chem. Abs.*, 1931, 25, 4722.



## Chapter 70

# Testing of Synthetic Resin Coatings

In this chapter, the tests for synthetic coatings will be described in general terms, the object of the examination will be pointed out, wherever possible interpretations of the results will be given and references will be cited for the exact procedures. General tests are given first, covering the methods used in determining physical properties, curing characteristics and aging tests, followed by the more specialized methods.

### SPECIFIC GRAVITY

In determining the specific gravity of a varnish, use may be made of a pycnometer, a Westphal balance or a hydrometer so graduated that the values can be determined within a tenth of a per cent. It is quite essential that the temperature of the varnish be kept constant and determinations should be made at  $20 \pm 0.5^\circ\text{C}$ . For most work the results should be reduced to a temperature of  $20^\circ\text{C}$ . In general it will suffice to apply a correction of 0.0007 per  $1^\circ\text{C}$ . to be subtracted from the observed value for temperatures below  $20^\circ\text{C}$ . and added for those above that point.

### VISCOSITY

Viscosity may be determined either relatively or absolutely. For relative determinations use can be made of a set of viscosity tubes such as are quite generally employed in the varnish industry for comparison and control work. The temperature of the varnish should be maintained within  $0.5^\circ\text{C}$ . while observations are being made. For such work a graduated pipette which is capable of giving reasonably accurate values would be permissible, but even with these indirect methods, the instrument should be calibrated for satisfactory results. Oils of known viscosity for determining the constants of such apparatus can be obtained from the U. S. Bureau of Standards.

If the above instruments are standardized, it is possible, by the use of correction factors, to express the coefficients in absolute units, that is, poises or centipoises.<sup>1</sup> For the measurement of viscosity reference should be made to the A. S. T. M. methods.<sup>2</sup> Some instruments, such as the MacMichael viscosimeter, are calibrated by the manufacturer so that the viscosity can be read directly in poises or centipoises. The Höppler viscosimeter, which was demonstrated before the World Petroleum Conference in London, 1933, also has many advantages. This instrument consists of a precise-diameter glass tube set at an angle of  $70^\circ$  to

<sup>1</sup> The absolute viscosity in c.g.s. poises has been defined as the force in dynes required to move, at a velocity of one centimeter per second, a square centimeter surface past another parallel like surface one centimeter away, overcoming the resistance to shear of the intervening liquid. The absolute viscosity for water at  $20^\circ\text{C}$ . is approximately 1.0 centipoise.

<sup>2</sup> A.S.T.M., *Tentative Standards (D115-31T)*, 1931.

the horizontal, surrounded by a water jacket so that the temperature may be controlled within narrow limits. Supplied with this tube are gold-plated steel balls which are somewhat smaller than the internal diameter of the tube. The diameters of these balls are graduated, and the proper selection depends upon the viscosity of the liquid to be treated. Since the ball is almost the same diameter as the tube, the flow of the liquid in the annular space between the tube and ball is laminar, preventing disturbances due to turbulence. The ball selected for the determination is the one which will require at least 6 times as many seconds to fall through a prescribed distance on the tube as this distance is in centimeters. The apparatus has the peculiar advantage of being adaptable to determinations on gases, liquids or materials of viscosities as high as 1,000,000 centipoises. It can even be used with substances that are not transparent as one can note the position of the ball when it touches the glass on the rear of the fall tube.

#### FLASH POINT

The flash point of a varnish is that temperature at which the vapor above the liquid ignites upon the introduction of a flame. In determining this characteristic, a definite quantity of the specimen is placed in a specially designed closed vessel, and the temperature of the varnish is gradually raised at a specified rate by heating the surrounding bath. This procedure has been standardized by the A. S. T. M.<sup>a</sup>

#### TIME OF CURING

The determination of the time of curing is especially valuable in the case of varnishes used to impregnate cloth or paper. These materials are cured in a press under the influence of heat and pressure, thus forming a finished laminated board. The time required to cure a varnish resin is of importance since the entire processing of phenol resin and urea resin laminated materials depends upon this quality. The time of curing is defined as the time which is required to transform the resin contained in the impregnated cloth from the soluble fusible state to the infusible form. Such treatment changes the loose pile of sheets of impregnated material into a compact, rigid mass. The stiffness of a molded plate depends upon the thickness of the product, the type of varnish employed and the percentage of varnish and filler.

As a measure of the time of cure of phenolic resins, use can be made of the determination of a state of the varnish or resin known as the "End Point." After heating for a certain length of time, at a predetermined temperature, it will be found that the varnish no longer flows from the stirring rod but instead clings, exhibiting much the behavior of a piece of over-stretched rubber. When this occurs the end point has been reached. The period during which the varnish has to be heated under the definite conditions of temperature in order to reach this state is known as the "Set Time." A convenient method of making this determination is as follows: Ten cubic centimeters of the varnish are placed in a vessel having a bottom area of 20 square centimeters and a height of 8 to 10 centimeters. This container is placed in a steam jacket so that it may be kept at a temperature of 135°C. The varnish is stirred during heating and the interval required to reach the end point is taken as the set time.

The vessel used in this test should have a cover with an opening not larger

<sup>a</sup> A.S.T.M. Standards (D66-31), 1933, II, 805.

than twice the diameter of the stirring rod. It should be borne in mind that in making comparisons of different varnishes or even of the same varnish having different solvents, values may vary because of the difference in time required to evaporate the vehicle, since this must be done before the varnish starts to cure appreciably.

#### PERCENTAGE OF NON-VOLATILE MATTER

Since the essential action of a given varnish depends upon the non-volatile constituents, it is of considerable interest to the consumer to know the proportion of solvent and base in the product.

The non-volatile matter by weight may be determined in the following manner: A small sample of the material is placed in a beaker approximately eight centimeters in diameter and carefully weighed. The container and varnish are then heated for three hours in an oven at  $110 \pm 1^\circ\text{C}$ . The dish and residue are then cooled, preferably in a desiccator, and accurately weighed. Knowing the weight of the beaker and resin, and of the dish alone, the weight of the residue can be found. The ratio of the residue to the original sample by weight represents the percentage of the non-volatile matter. For comparative work it is essential that the same weight of varnish be taken each time and that identical receptacles be used in all determinations.

Users of phenolic type of varnish who impregnate cloth or paper and then press it into boards, or other shapes, are interested in knowing the volatile content of the impregnated material before it is pressed. To make this determination a piece of cloth or paper is cut from the sheet after it has been impregnated and passed through the drying tower but before it passes around the final roll. This piece is accurately weighed, heated for 10 minutes at  $160^\circ\text{C}$ . and reweighed. In both cases sufficient time is allowed for the sample to cool to room temperature, preferably in a desiccator. From the masses determined by the two weighings the percentage of volatile matter given off is known. Then from the average mass of a sheet of the unimpregnated paper or cloth of the same size as the sample tested, the non-volatile matter by weight can be obtained. Unfortunately, no standards have been adopted as to the temperature at which the sample should be heated nor as to the exact length of time of treatment. It therefore falls upon the consumer to ascertain for himself the most suitable limits of time and temperature for his purposes. Eventually, the exact procedure will be definitely established, but it may be that different temperatures and times of heating will be found necessary for different classes of materials. In making this test care must be taken to see that the resin is not polymerized, that the solvent is driven off and that the moisture content of the paper or cloth is not materially changed. Lower temperatures may be used when the resin is easily polymerized.

It is sometimes of interest to determine the volume percentage of solvent in a varnish and thus arrive at the composition of the varnish with respect to solvent and base constituents. This information may be secured by distilling 100 cc. of the varnish.<sup>4</sup> For phenolic varnishes the distillation should be carried on until the volatile distillate comes over slowly, or until the residue begins to gel. Care must be exercised not to raise the temperature too high and thus carry the process too far.

The specific gravity of the volatile matter recovered by the distillation may then be found by one of the usual methods. Likewise the specific gravity of the

<sup>4</sup> Method of Test for Distillation of Gasoline, Naphtha, Kerosene and Similar Products, *A.S.T.M. Standards*, (D88-50), 1933, II, 778.

original varnish should be determined. The percentage of the volatile matter by volume is then given by the formula

$$X = \frac{AC}{B}$$

X—the percentage of volatile matter by volume.

A—the specific gravity of the original varnish.

B—the specific gravity of the volatile matter recovered by the distillation.

C—the percentage of volatile matter by weight as determined above.

#### TIME OF DRYING

The procedure for this test as adopted by the American Society for Testing Materials<sup>5</sup> specifies the use of pieces of brass or copper, about 4 centimeters wide and 20 centimeters long, thoroughly cleaned and polished. The strip is dipped into the varnish at room temperature and is withdrawn uniformly at the rate of 38 centimeters per minute. The consistency of the varnish should be such that when dry the thickness of the film on each side of the metal strip will be between 0.022 and 0.026 mm. For air-drying varnishes, the film is dried in a dust-free atmosphere at 20°C. In the case of baking varnishes, the specimens are dipped and allowed to drain at room temperature until the varnish is set. The coating may be said to have set when a finger print made by lightly pressing at a point two inches from the bottom of the panel will not become obliterated by further flow. It is then dried in an oven at 110±1°C. The specimens are taken from the oven at intervals and tested for dryness. A suggested time for the removal of the first sample is thirty minutes. The others may be tested at intervals of 10 minutes. The varnish is considered to be dry when a piece of kraft paper 38 mm. wide, 152 mm. long and approximately 0.063 mm. thick does not adhere when pressed against the coating for one minute by a cylindrical one-pound mass one inch in diameter. The paper is applied near the center of the specimen and at right angles to the length. This is done at room temperature after the specimen has cooled. In the case of varnishes which dry "tacky," the time of heating must be continued until the resistance to removal of the paper appears to have become constant.

Wolff<sup>6</sup> has pointed out that in determining drying time of varnishes it is necessary to use care that exactly similar conditions are obtained. This is especially true in the case of relative humidity. He points out that a given finish which required 10 hours to dry in air at 40 per cent relative humidity needed 13 hours at 70 per cent and only dried after 20 hours at saturation. Another, however, required 11 hours at 40 per cent humidity, 12 hours at 70 per cent and 14 hours in saturated air, so that it is impossible to establish any relationship between drying time and humidity. Wolff applied a piece of clean paper to the film after definite intervals of time and obtained his values by measuring the force required for separation.

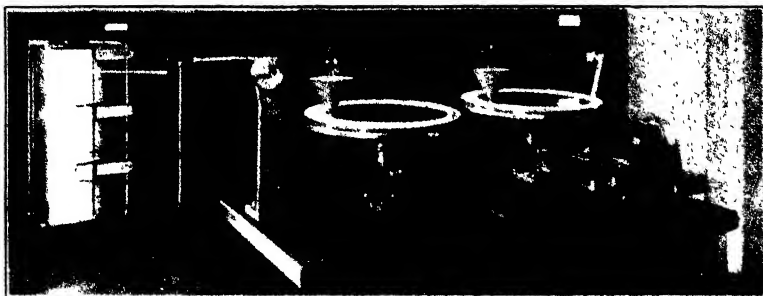
A simple device for determining the drying time of paints and varnishes<sup>7</sup> employs glass or rubber tips placed at the end of a balance arm. These are impressed upon the coating with a definite load. When the glass tip does not pick up the film, the material is set, and when the rubber tip does not mar the surface, as the specimen is drawn along under it, the film is considered dry.

<sup>5</sup> A.S.T.M. *Tentative Standards (D115-31T)*, 1933, 816.

<sup>6</sup> H. Wolff, *Farben-Ztg.*, 1924, 29, 574; *J.S.C.I.*, 1924, 43, 303.

<sup>7</sup> F. N. Stearns, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1932, 423; *Chem. Abs.*, 1932, 27, 614.

Sanderson<sup>\*</sup> has also described a satisfactory way of determining this value. A disc, carrying a specimen film, is placed on a slowly rotating vertical shaft. As the coating is revolved, sand flows upon it in a small stream describing a spiral, since the point at which the particles strike the film gradually moves towards the center of the plate. The varnish has dried dust-free when the sand no longer adheres to the surface. Knowing the speed of rotation of the disc, usually one revolution every three hours, the length of the spiral measures the period elapsed.



Courtesy J. McE. Sanderson

FIG. 204.—Drying-Time Meter. Also shown are instruments for recording humidity, temperature and atmospheric pressure.

Gardner<sup>\*</sup> has made suggestions regarding the utility of certain grades of synthetic resins for the manufacturing of quick-drying varnishes, and he gives the results obtained through the use of these materials in the production of various grades of coatings.

#### HEAT ENDURANCE

To test the resistance of a finish to heat, a thoroughly cleaned sheet of copper or brass 20 cm. by 3 cm. by 0.127 mm. thick is used.<sup>10</sup> The specimen to be examined should be of such consistency that the dry film will have a thickness between 0.022 mm. and 0.026 mm. In preparing the film the metal strip is dipped twice into the varnish in opposite directions and withdrawn at the rate of 38 centimeters per minute. The varnish at the time of applying the coating should be at a temperature of about 20°C. and the time between the first and second coats must be long enough so that the first coat is properly dried. After the second coat is hard, as determined by the drying time test, the specimens are heated in an oven at a temperature of  $110 \pm 1^\circ\text{C}$ . At the end of each 24-hour period a specimen is removed and bent around a rod an eighth of an inch in diameter. The heat endurance of the varnish is taken as the number of hours of heating in a well-ventilated oven at  $110^\circ\text{C}$ . at which the film shows the first signs of cracking upon distortion.

#### OIL RESISTANCE

To determine the ability of a varnish to withstand the action of oil, a specimen film is prepared in the same manner as for the preceding test. The samples are

<sup>\*</sup> J. M. Sanderson, *Proc. Am. Soc. Testing Materials*, 1926, 26 (3), 556; *Chem. Abs.*, 1927, 21, 1363.

<sup>\*</sup> H. A. Gardner, *Circ. Am. Paint, Varnish Mfrs. Assoc.*, 1926, 279; *Chem. Abs.*, 1926, 20, 3354.

<sup>10</sup> A.S.T.M. *Tentative Standards (D115-31T)*, 1934.

then dipped into a typical transformer oil at a temperature of  $110 \pm 1^\circ\text{C}$ . for 48 hours. The panels are duly removed from the oil and the effect of the hot oil on the varnish film examined. Sometimes the disintegration of the varnish film can be detected from the turbidity of the oil. This can be observed by holding two samples of the oil, one filtered and the other unfiltered, before a diffused light. Again if the disintegration is pronounced, it may be noticeable by a slight discoloration of the white cloth used in wiping off the excess oil from the specimens.

#### DRAINING OR WORKING VISCOSITY

The working viscosity of a varnish can be determined by the variation in thickness of the dried film from one end of the metal strip to the other after dipping and drying. A strip of brass or copper 35 centimeters long, 4 centimeters wide and 0.127 millimeter thick is immersed in varnish at  $20^\circ\text{C}$ . to within one inch of the top or to a definitely marked line and the strip is withdrawn vertically from the varnish at a rate of 38 centimeters per minute. The specimen is then hung vertically and permitted to drain at room temperature. It is dried or baked, according to the type of varnish, until dry. The thickness is then measured at say 2, 7 and 12 inches from the top of the strip. The differences between the thicknesses at the three points give a measure of the variation as a result of draining and constitute the data indicative of the draining or working viscosity.

#### ABRASION RESISTANCE

Numerous methods have been devised for the determination of the relative ability of coatings to withstand abrasive action. Gardner<sup>11</sup> has described one procedure that has been used to a considerable extent. This test employs a glass tube about 6 feet long having an internal bore of 0.875 of an inch. The tube is supported vertically immediately above the coated panel. The specimen is placed at  $45^\circ$  to the vertical, and the abrasive material, No. 50 emery powder, is dropped through the tube from a funnel having a bore of 5 mm. In striking the surface the emery covers an area of about one inch in diameter. The flow of abrasive is maintained until the finish is removed from the surface upon which it is applied. By means of a reservoir at the top and a scale holding the vessel into which the emery falls, the operation can be made continuous. When the film has worn through, the flow is stopped and the weight of emery that has fallen is obtained as a relative value of the wearing properties of the film. If the panel is colored before the application of the varnish, the point of complete abrasion will be more clearly defined. Some experimenters have specified an Ottawa sand such as is used for testing cement.<sup>12</sup> For this material a rate of flow of one liter per 150 seconds has been found satisfactory.

The method described by Schuh<sup>13</sup> in which sand is blown by means of an air blast against a rotating disc on which the film has been prepared has also proven to be a good measure of this quality. Wacholtz<sup>14</sup> has also evaluated the abrasion resistance of paints and varnishes by means of sand directed upon the film. Van Heuckeroth<sup>15</sup> studied varnishes from this standpoint. He worked with sand and determined the number of kilograms necessary to cut through a thickness of 25 microns of film.

<sup>11</sup> H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," *Inst. of Paint and Varnish Research*, 1927, 84.

<sup>12</sup> *A.S.T.M. Tentative Standards (D289-28T)*, 1933, 630.

<sup>13</sup> A. W. Schuh, *Ind. Eng. Chem., Anal. Ed.*, 1931, 3, 72.

<sup>14</sup> H. Wacholtz, *Farben-Ztg.*, 1933, 33, 180.

<sup>15</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 369.

## ADHESION OF LACQUERS AND VARNISHES

It has been found quite difficult to formulate a satisfactory method of determining the adhesion properties of varnish and paint films that will be of general application. Many suggestions, however, have been tried and used with a certain degree of satisfaction. Gardner has described a fairly satisfactory method. The varnish or lacquer is applied, by brushing, spraying, dipping or spinning, to thoroughly cleaned plates of black iron, glass or other materials, 3 by 5 inches. A piece of silk cloth is placed on the specimen while it is still tacky, and pressed down firmly. The surface is then cut into strips one centimeter wide with a razor, after sufficient time has been allowed for the film to dry. Next the test panel is fastened in a suitable tension machine, and the strips of cloth, having been loosened at the top and folded downward, are then pulled directly along the surface. The adhesion of alternate pieces is measured in this fashion and quite consistent results may be thus obtained.

Peters<sup>16</sup> has observed that phenolic varnishes were unsatisfactory when used for priming coats on aluminum. This statement applies only to baking varnishes. The heating of the coating was found to impair the mechanical properties of the metal as well as causing the film to lift away from the surface.

Van Heuckeroth<sup>17</sup> has determined the adhesive properties of films by observation after the sand abrasion test. He merely noted whether or not the film had pulled away from the surface of the glass plate before it was cut through by the sand. This test, of course, gives no clue as to the relative degree of merit.

## DURABILITY OF VARNISHES

Many investigators have sought to obtain a test, or series of tests, which would indicate the probable durability of varnished surfaces. A sub-committee of the American Society for Testing Materials<sup>18</sup> found that there were several tests that gave good results in the hands of various investigators, but that the kauri reduction method for determining the elasticity or toughness was perhaps the most satisfactory procedure so far developed. Pulsifer<sup>19</sup> has also used the kauri reduction method and agreed it gave the best estimate of the durability of a coating.

The kauri reduction test is carried out by proportionally reducing the elasticity of the varnish with a solution of No. 1 kauri gum. A quantity of small broken pieces of "run kauri" is heated in the presence of twice its weight of spirits of turpentine. Only that grade of spirit which is volatilized between 153 and 170°C. should be used. The purified gum may then be dissolved in turpentine at 149°C., adding enough solvent to replace that lost during distillation.

It is next necessary to determine the non-volatile content of the varnish under examination according to the method outlined in a previous section. After this is done, add 100 grams of the varnish to an amount of the prepared kauri solution equal by weight to 50 per cent of the non-volatile matter in the specimen. Having mixed this preparation thoroughly, a small metal test panel is coated as described in the test for determination of drying time. When the film has dried, it should be possible to bend the panel over a 3 mm. rod, the coating being on the

<sup>16</sup> J. Peters, *Metallics*, 1932, 22, 1469, 1501; *Chem. Abs.*, 1933, 27, 2316.

<sup>17</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 369.

<sup>18</sup> *Proc. Am. Soc. Testing Materials*, 1922, 22 (1), 375; 1923, 23 (1), 399.

<sup>19</sup> L. V. Pulsifer, *Proc. Am. Soc. Testing Materials*, 1923, 23, 282; *Chem. Abs.*, 1924, 18, 1203.

convex side, without cracking the film. For purposes of comparison it may be desirable to find the greatest percentage of kauri gum, calculated on the basis of the non-volatile material in the varnish, which may be added without rupturing the surface when bent over a 3 mm. rod.

Harrison<sup>20</sup> has observed the durability of some paints on wooden test panels that have been treated with preservatives repellent to termites. Red wood, western yellow pine and Douglas fir were impregnated with preservatives known as AC-Zol, Anaconda neutral, Bruce 5A, Halowax, Lignophol, Triolith, zinc chloride and zinc meta-arsenite. Three priming coats were used: aluminum bronze in mixing varnish, aluminum bronze in synthetic resin varnish and white lead-zinc oxide exterior paint which had been reduced with turpentine. White lead-zinc oxide raw linseed oil paint was used for the second and third coats. In addition the Halowax-treated wood received a Bakelite-type primer followed by the above-named top coats and finally by a white lead-zinc oxide Bakelite paint. The conditions of the tests after 6 and 12 months are given in detail. With the exception of Bruce 5A, all the preservatives permitted painting. The durability of the paint on zinc chloride treated wood was less than in the other cases. The first two priming coats mentioned gave better results than the last. The species of wood had no apparent effect.

Pearce<sup>21</sup> has made an extensive study of the relationships of physical tests and chemical composition with respect to durability. He has shown that the kauri reduction values are in good agreement with the results given by exposure data. Gardner<sup>22</sup> has presented the results of exposure tests upon several different samples of varnish, and also the results of various methods such as the kauri reduction test. This worker found that the kauri reduction test paralleled results obtained through actual service. In later work Gardner<sup>23</sup> found that the durability of spar varnishes was not improved by the addition of antioxidants such as pyrocatechol, quinol, heptene and two rubber accelerators.

Stearns<sup>24</sup> has also observed 20 typical varnishes using kauri reduction and regular exposure tests. For the older types of varnish the kauri reduction test does indicate durability, but among certain newer types it seems to fail, as for instance it has been reported in the case of one type of phenolic resin, better durability was associated with lesser kauri reduction values.

Levy<sup>25</sup> has ascertained that the kauri reduction test does not give reliable indication as to durability in the case of varnishes made of alkyd and some phenolic types of resins. Information on embrittlement may be obtained by using arc-lamp irradiation. This method was employed by Wilson<sup>26</sup> in connection with pure sheet rubber as a substratum for his varnished test pieces.

Kolke<sup>27</sup> determined the durability of coatings on phosphatized and untreated iron. When the panels were prepared half the metal surface was sanded, and then half the sanded portion and half the unsanded portion were phosphatized. The coatings used were shellac, bituminous varnish, synthetic resin spirit varnish and synthetic resin-tung oil varnish. These were exposed to salt water spray for four weeks. In general the durability was greatest on the sanded phosphatized surfaces, next on the phosphatized only, next on sanded and last on the untreated surfaces.

<sup>20</sup> A. W. C. Harrison, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1931, 404, 407.

<sup>21</sup> W. T. Pearce, *Ind. Eng. Chem.*, 1924, 16, 681.

<sup>22</sup> H. A. Gardner, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1926, 260.

<sup>23</sup> H. A. Gardner, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1932, 410, 135; *Chem. Abs.*, 1933, 27, 77.

<sup>24</sup> F. N. Stearns, *Am. Paint J.*, 1932, 16 (53A), 21. *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1933, *Chem. Abs.*, 1933, 27, 614.

<sup>25</sup> S. A. Levy, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1932, 410, 146; *Chem. Abs.*, 1933, 26, 3999.

<sup>26</sup> J. H. Wilson, *Bur. Standards J. Research*, 1931, 7, 73; *Chem. Abs.*, 1931, 23, 5999.

<sup>27</sup> F. Kolke, *Farben-Ztg.*, 1932, 37, 928; *Chem. Abs.*, 1932, 26, 331.



## KAURI-BUTANOL TEST

The kauri-butanol test is frequently employed to evaluate various solvents which might be employed in varnishes. Briefly, the test consists of titrating 20 grams of gum kauri solution with the solvent to be tested in a 200 cc. Erlenmeyer flask. The kauri solution as used here is prepared by dissolving 100 grams of gum kauri in 500 grams of normal butanol. The end point is reached when the normally clear liquid acquires a slight turbidity. This may be determined by placing a printed page beneath the flask, and noting when the print, as viewed through the solution, just becomes blurred. The number of cubic centimeters of solvent required to produce this end point is the kauri-butanol value of the solvent. When the kauri solution is properly prepared, titration with C.P. benzene will give a value of 100.

Sweeney and Tilton<sup>22</sup> have reported on the results given by this procedure as applied to hydrogenated solvent naphthas.

## EXPOSURE TESTS

Exposure tests are designed to secure information concerning the probable durability of a varnish if it were in actual service. The test is employed to give results more readily than would be the case if the material were put in actual service. The exposure is so made as to subject the materials, if possible, to the most severe conditions found in the service for which it is intended. Thus one specimen may be subjected to heat and cold alone, another sprayed with hot and cold water, and still others may be weathered under normal conditions of rain, wind, snow and sun.

Walker<sup>23</sup> has pointed out the importance of position in weather tests. He finds that panels should be set at 45° to the horizontal facing south in the latitude of Washington, D. C. This angle should be varied according to geographical position and should be the same as the latitude of the locality.

Arnold<sup>24</sup> has described some exposure tests made in the woods of Brazil over a period of a year. All varnishes of the ordinary type showed stickiness for considerable time. Varnishes containing synthetic resin did not yield this unfavorable result.

Gardner<sup>25</sup> has given a description of accelerated laboratory tests for paints and varnishes. Exposure to ocean air showed phenolic and modified phenolic oil varnishes to give generally satisfactory results as compared with many coatings. Rapid failure was shown by sulphur-treated varnishes, lead tungstate liquids, boiled linseed oil, gloss oil and a water-resistant rubber varnish.

Van Heuckeroth<sup>26</sup> gives a number of results for various resin finishes which were flowed out upon black iron panels that had previously been primed with an oleoresinous coating pigmented with equal parts of Indian Red and zinc chlorate. These coatings were baked for two hours at 240-250°C. and then rubbed. The panels were duly exposed on racks facing south at 45° to the vertical. The number of days for the first and also for the final failure were noted. The latter period was arbitrarily set at the time when the film did not protect 50 per cent of the surface.

<sup>22</sup> W. J. Sweeney and J. A. Tilton, *Ind. Eng. Chem.*, 1934, 26, 693.

<sup>23</sup> P. H. Walker, *Ind. Eng. Chem.*, 1924, 16, 828.

<sup>24</sup> Arnold, *Chem. Ztg.*, 1932, 56, 55; *Chem. Abs.*, 1932, 26, 2606.

<sup>25</sup> H. A. Gardner, *Ind. Eng. Chem. Anal. Ed.*, 1932, 4, 94.

<sup>26</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 369.

## ACCELERATED WEATHERING TESTS

Since the accumulation of data by normal exposure is extremely slow, there has been much interest in the development of accelerated tests designed to secure comparative results in a relatively short time. Gardner<sup>22</sup> has reviewed the details of the developments of this type of test. As innumerable combinations of artificial conditions are possible only a few of the fundamental principles involved in accelerated testing cabinets will be described here.

**Carbon Arc Exposure Cabinet.** In this cabinet, panels 5 by 10 inches with specimen coatings are set upon a flexible rack. These are exposed to two carbon arc weatherometers which revolve once every thirty minutes, being followed by alternating sprays of water. The panels are placed approximately 8 inches from the lamp globes and reach a temperature of 140°F., after which they are cooled to approximately 70° by the water. This accelerated test obtains, in about 300 hours, results that would require at least three to six months under standard conditions of service.

**Mercury Tube Test Cabinet.** In a cabinet of this type use is made of a quartz tube mercury vapor lamp. The source of light is mounted horizontally at the axis of a drum revolving horizontally. The panels to be exposed are placed upon the inside of the drum in such a way that the lower section may be immersed in water.<sup>24</sup>

## FLEXIBILITY

The following procedure has been found to be of considerable value in classifying varnishes as to flexibility. An H28 gage aluminum plate is coated to such a thickness that one ounce of varnish, based on the dry weight; would be used per square yard. The plate is hung in a well-ventilated drying room, after which it is baked at 100°C. for two hours and finally allowed to cool for half an hour. It should then be bent at an angle of 180° over a quarter inch rod. A durable varnish will exhibit no cracks after this treatment.

Schuh<sup>25</sup> has used a mandrel test for flexibility in which he has elaborated slightly on the customary procedure. His instrument permitted metal panels up to thicknesses of  $\frac{1}{16}$  inch to be bent about any one of six rods varying in diameter from  $\frac{1}{8}$  inch to 1 inch, in such a manner that the panels followed closely the contour of the mandrels. The smallest diameter bend permitted without fracture is then a measure of flexibility.

## GLOSS MEASUREMENT

Reference should be made to the discussion of this subject in Chapter 69, as the fundamental principles embodied in the determination of the gloss of a varnish film are the same as for the surface of laminated or molded phenolic materials. Bolme<sup>26</sup> has made some special tests which he believes are of considerable practical value. His method is based upon comparisons between the reflection given by the specimen surface as contrasted with those of a series of standard coatings of nitrocellulose lacquer. The latter are prepared by mixing a flattening paste with a clear

<sup>22</sup> H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," *Inst. of Paint and Varnish Research*, 1927, 309.

<sup>23</sup> For a correlation of accelerated tests see *Am. Paint Journal, Convention Daily*, 1931, Dec. 4.

<sup>24</sup> A. E. Schuh, *Ind. Eng. Chem. Anal. Ed.*, 1931, 23, 1846.

<sup>25</sup> S. Bolme, *Am. Paint J.*, 1932, 16 (53A), 8. *Paint, Oil, Chem. Rev.*, 1932, 94 (10), 47. *Circ. Am. Paint, Varnish Mfrs. Assoc.*, 1933, 423; *Chem. Abs.*, 1933, 27, 613.

lacquer. The reflected object appears as a translucent white field with black cross bars, and the reflected field can be held in definite relation to the standards and specimen.

#### HARDNESS OF VARNISH FILMS

Gardner and Parks<sup>27</sup> have made a review of the older methods of testing the hardness of films, including the Laurie-Baily, the Clemens and the weighted pencil point scratch method. They have given photographs of the scratches produced together with a tabulation of the results obtained.

Walker and Steele<sup>28</sup> of the U.S. Bureau of Standards have determined hardness by the use of a swinging beam pendulum. The apparatus employs a beam whose fulcrum is a ball, pivoting on a specimen of the varnish film prepared on a base plate. The method consists of oscillating the beam through a chosen amplitude while the ball is resting on the specimen film. The time required for the pendulum's amplitude to decrease to one half its original value is compared with the same quantity when the ball of the balance is resting on a piece of smooth glass as a standard surface. Van Heuckeroth<sup>29</sup> has also used this type of instrument.

Laurie<sup>30a</sup> has employed a device constructed much after the manner of a Westphal balance. The long arm carries a point on the underside and a pan on the top. The test film is prepared on glass. The weight required to scratch the film is noted as well as the nature of the scratch. When the scratch is ill-defined or can be erased by rubbing, the film is harder than the crystal used as the scratching medium.

Wolff has suggested a method similar to Laurie's procedure except that a knife blade is substituted for the point. The sample is carried on a car and moved at a definite speed under the blade, and the weight required to mar the surface is noted. This test requires that the film be of uniform thickness.

Wolff and Wilborn<sup>30</sup> have pointed out some of the merits of the pencil method of determining hardness of films and have also outlined a way of overcoming the difference in pressure applied when making the test. The process involves placing the varnished panel to be tested in one pan of a balance, and loading the other pan with a definite weight. Only sufficient pressure is exerted during the test to ensure equilibrium. The surface is consequently held up against the moving point by a definite force. In a revised method outlined by Wilkinson<sup>31</sup> pencils of different grades were drawn across the film until one hard enough to cut the film was found. It was stated that the results were practically independent of the pressure used in applying the pencil point.

Löwa<sup>32</sup> has measured the difference in hardness of films which had been pigmented with white lead, ferric oxide, zinc oxide, titanium oxide and graphite respectively. Marked differences were observed between the films kept inside and films exposed to the weather at 45° facing south. Of the indoor films the graphite paint showed the greatest loss in hardness, while in exposure tests it suffered the least.

<sup>27</sup> H. A. Gardner and H. C. Parks, *Circ., U. S. Paint, Varnish Mfrs. Assoc.*, 1925, 228, 195. See also R. S. Dantuma, *Chem. Weekblad.*, 1934, 31, 432; *Chem. Abs.*, 1935, 29, 202.

<sup>28</sup> P. H. Walker and L. L. Steele, *Circ., U. S. Paint Mfrs. Assoc.*, 1925, 229, 207; *Chem. Abs.*, 1925, 19, 1733. See also H. A. Gardner, "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," *Inst. of Paint and Varnish Research*, 1927, 70.

<sup>29</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 369.

<sup>30a</sup> A. P. Laurie, *Oil Colour J.*, 1908, 33, 453; *Chem. Abs.*, 1908, 2, 2020. A. P. Laurie and F. G. Baily, *J. Roy. Scott. Soc. Arts*, 1906, 17, 101; *British P.* 3438, 1906; *J.S.C.I.*, 1906, 25, 819; 1907, 26, 159.

<sup>30</sup> H. Wolff and F. Wilborn, *Farben Ztg.*, 1929, 34, 2731; *Brit. Chem. Abs. B*, 1929, 825.

<sup>31</sup> J. A. F. Wilkinson, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1923, 184, 372.

<sup>32</sup> A. Löwa, *Farben Ztg.*, 1932, 38, 100.

Wilkinson<sup>42</sup> has described a modified form of the swinging-beam hardness apparatus in connection with a discussion on physical examinations of paints.

Sward<sup>43</sup> has proposed an apparatus for testing surface hardness that is composed of rocker arms carrying a weight, a means of shifting the center of gravity of the weight, a pendulum operated by the rocker arms from a point directly above the weight, and a scale co-operating with pendulum for measuring the angle of deflection. The apparatus is rocked backward and forward and the angular movement noted. The harder the surface, the greater will be the angle of movement.

Sheppard and Schmitt<sup>44</sup> have given a detailed description of a method used to determine resistance to scratching, which has the advantage of giving quantitative results. It was employed in connection with studies of cellulose derivatives but it is capable of general application. The equipment consists of a scratch dynamometer and an instrument for observing the cut. The dynamometer can be arranged to give a single scratch, made by an increasing load or, if preferred, a series of scratches, each employing a constant pressure. The width of the cut may then be measured, and it is also possible to accurately observe its appearance.

Banks<sup>45</sup> has recommended that a moderate sized sample of varnish be placed in a glass container and examined from time to time for the formation of a skin. Preferably, the specimen should be kept in a dark room to simulate the conditions under which it would be stored in the usual metal can.

#### DIELECTRIC STRENGTH IN DRIED STATE

A dielectric strength test has been formulated to determine the practicability of a varnish for impregnating cloth or paper. While the test is only relative and does not give the actual dielectric strength of the varnish alone, it does give the dielectric strength of the treated material as normally used. Specimens of kraft paper 20 cm. square and 0.076 mm. thick are impregnated by double dipping, once in each direction in accordance with the procedure given for the drying time test. The specimens should be dried for a period exceeding several times that required for the determination of the drying time. After being dried, the sample is then placed between electrodes which should be of circular form, two inches in diameter. The edges of these discs must be rounded, preferably to a radius of 0.75 cm., as failure will otherwise take place around their circumferences and give misleading results. The transformer used should be of such a type that the potential may be raised at the rate of 500 volts a second.

The dielectric strength should be determined under three separate conditions:

- (a) At room temperature (approximately 20°C.) in air.
- (b) At 75°C. in air.
- (c) At room temperature on specimens which have been immersed in water for a period of 24 hrs.

If the tests are also run under oil at 20 and 75°C. this fact should be definitely stated as results obtained in oil will not agree with those found when the specimen is surrounded by air.

Since the dielectric value of the impregnated material does not appear to bear very direct relationship to the strength of the paper employed it is not usual to determine this value before treatment.

<sup>42</sup> J. A. F. Wilkinson, *J. Oil, Colour Chem. Assoc.*, 1932, 15, 259; *Chem. Abs.*, 1933, 27, 197.

<sup>43</sup> G. G. Sward, U. S. P. 1,938,752, Nov. 21, 1933; *Chem. Abs.*, 1934, 28, 918.

<sup>44</sup> R. E. Sheppard and J. J. Schmitt, *Ind. Eng. Chem. Anal. Ed.*, 1933, 4, 302.

<sup>45</sup> L. M. Banks, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1932, 432; *Chem. Abs.*, 1933, 27, 614.

In determining the dielectric strength of dipping, brushing and spraying varnishes it is desirable that they be tested under as many conditions as possible. This is due to the fact that a comparison of the values given by a single varnish under various treatments is of importance.

#### DIELECTRIC STRENGTH IN THE LIQUID STATE

If a coating is to be used for insulating purposes an examination of its dielectric strength as a fluid becomes of interest since such procedure will indicate the presence of water or foreign matter in the material. However, this test can not be applied to varnishes whose solvents are poor insulators as for example alcohol.

The container used for this work should be a oil test cup made of a material having high dielectric strength. The electrodes are preferably flat discs one inch in diameter and so mounted in the cup that a gap of 0.10 inch can be accurately maintained between them. The electrodes should be at least 1.5 cm. below the surface of the varnish during the test.

#### RESISTIVITY

**I. Volume Resistivity under Normal Conditions.** In order to determine the volume insulation resistance of varnish for dielectric purposes, the samples can be prepared on copper or brass strips such as are used for the preparation of the specimens for drying time examination. The test pieces, however, must be dipped and dried twice so as to develop a greater thickness of coating. The final drying period should be the same length as that employed for the preparation of the samples under dielectric strength. Electrodes two centimeters in diameter may then be painted, using a conducting coating, such as aluminum bronze, at various places over the surface, no two electrodes being placed nearer than three centimeters on centers. The resistance between each of these electrodes and the brass or copper plate can then be measured by a galvanometer.\* Knowing the area of the electrodes, the thickness of the varnish film, the current flowing through the varnish as indicated by the galvanometer circuit, and the current flowing through a standard resistance, say, one megohm, the resistivity per unit volume may be determined.

The calculation of the volume resistivity of the film is made as follows: The volume resistance,  $R$ , in ohms, is calculated from the equation

$$R = \frac{MDS}{D'S'}$$

where

$M$ =value of calibrating resistance in ohms.

$D$ =deflection of galvanometer, in any system of units, with the calibrating resistance only in the circuit.

$S$ =shunt ratio when calibrating resistance is measured.

$S'$ =shunt ratio when sample is being measured.

$D'$ =deflection of galvanometer with sample in the circuit in the same units as " $D$ ."

\* *A.S.T.M. Tentative Standards, (D267-32T), 1932, 885.*

The unit resistivity in ohms per cubic centimeter,  $C$ , may be calculated from the formula

$$C = \frac{RA}{T}$$

where

$R$ =volume resistance in ohms as found from the preceding equation.

$A$ =area of the small painted electrodes in square centimeters.

$T$ =thickness of the varnish coating in centimeters.

This does not take into consideration the edge effect, but since the film is very thin as compared with its area the error involved is scarcely worth taking into account. Certainly the proportionate magnitude of discrepancy due to this cause is less than that introduced in the physical measurement of the thickness of the varnish film.

**II. Surface Resistivity under Normal Conditions.** The determination of the surface resistivity of dried varnishes differs from the preceding examination in some particulars. The specimen must be prepared on a non-conductive base such as glass or fused quartz. Two metal strips, 10 cm. long, spaced parallel to each other at a distance of 1 cm., are placed upon the coating. In some cases it may be found more convenient to press strips of tin foil into the varnish before drying to insure intimate contact with the electrodes. Employing a galvanometer circuit, the total resistance between the electrodes may again be calculated from the formula given in the preceding section.

$$R = \frac{MDS}{D'S'}$$

Then the unit surface resistivity,  $\rho$ , or the resistance between the two opposite sides of a square will be obtained from the expression

$$\rho = \frac{RL}{B}$$

where  $R$ =resistance in ohms as found above.

$L$ =length of the electrodes in centimeters.

$B$ =distance between electrodes in centimeters.

It is often necessary to measure the effect of humidity on a varnish film at moderate temperatures since this condition is frequently found in service and also because varnishes will show considerable differences when subjected to moist atmospheres. While complete equilibrium is not reached in all cases even after an exposure of four days to humid conditions, the resistivity has been so lowered by such treatment that it gives a good measure of the insulating property of the film. Hence after the samples are prepared they can be exposed to the desired degree of moisture in closed vessels for the length of time desired. Proper conditions of humidity may be produced by choosing the appropriate salts for use in the desiccator, or by selecting a sulphuric acid-water solution of the proper density. The salt solutions are the more satisfactory since the humidity is not affected by the conditions of moisture of the specimens. A supersaturated solution of common salt,  $\text{NaCl}$ , will give an atmosphere of 75 per cent relative humidity, while a 90 per cent relative humidity may be obtained by use of a solution of potassium nitrate in water having an excess of salt present. Or, if one cares to do so, he may obtain

any desired condition by mixing dried air and saturated air in different proportions by a bubbling process.

The determination of the effect of humidity on the surface resistivity of varnish films can be measured while the film is exposed to the humid conditions if proper care is exercised. The samples, having been prepared as mentioned in the test for surface resistivity under room conditions, are placed in closed vessels having the desired humidity. By running leads into the receptacle through carefully insulated sections, the resistivity measurements may be taken as desired. Care must be used, however, to protect the surfaces on the inside of the humidity chamber so that the measuring leads will not take up moisture. If the inside of the container between these leads is well coated with crude ceresin or ozokerite, little difficulty will be experienced in making the measurements, and error due to leakage will be minimized.

#### POWER FACTOR AND DIELECTRIC CONSTANT OF VARNISH FILMS

The specimens for use in power factor measurements are prepared on metal strips in accordance with the methods used for drying time tests. Electrodes can then be placed on the surface. A convenient method is to apply tin foil with a small quantity of vaseline or to paint the conductive areas on the sample with aluminum bronze. It is only necessary to apply one electrode, however, as the copper or brass base plate will serve for the other side of the circuit. The size of the terminals should be adjusted to yield the capacitance desired in order to make the power factor measurements with the apparatus available. Diameters of two centimeters or more will ordinarily give adequate capacitance. The usual methods of measuring power factor at frequencies of 60 cycles, 1000 cycles and 100 to 1500 kilocycles have already been described in Chapter 69.<sup>44</sup>

#### WATER ABSORPTION OF VARNISHES

Stoppel<sup>45</sup> has carried out water absorption tests on carefully prepared panels of basswood protected with four coats of various varnishes, the elasticities of the films having been previously determined by the kauri reduction method. It was stated that the permeability of the film decreased with increased thickness, that it decreased with an increase in the proportion of resin in the varnish and that it decreased as the whitening of the film decreased when the usual water test was employed. This worker also showed that a varnish which was highly impermeable to water when fresh lost this property upon exposure. It would appear that the permeability of all varnishes to water decreases during exposure until cracking occurs, at which time it obviously would increase very rapidly. Water apparently does not penetrate a varnish film through pores but is dissolved and then absorbed by the under body, hence whitening of a film may be attributed to supersaturation of the coating.

Van Heuckeroth<sup>46</sup> has determined the water permeability of the films which he studied by two methods. The coatings were first prepared by spinning lacquer upon amalgamated tin panels, drying and then stripping off the film. By his first method, 10 grams of water were placed in a four-ounce screw-cap container. The tops of the jars were then cut out so as to form an opening 3 cm. in diameter. The film was extended over the top of the jar and the perforated cap screwed into place. The joint between the cap and the jar was sealed with wax, and the

<sup>44</sup> A.S.T.M. *Tentative Standards*, (D150-34T), 1934, 34.

<sup>45</sup> E. A. Stoppel, *Proc. Amer. Soc. Testing Materials*, 1924, 24, 455; *Chem. Abs.*, 1925, 19, 1783.

<sup>46</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 369.

containers were placed in pint jars containing approximately 50 cc. of concentrated sulphuric acid. The amount of moisture passing through the film was then determined by periodic weighings.

In the second test, the migratory tendency of the water was reversed. Ten grams of calcium chloride in jars were put in external containers in which 50 cc. of water had been substituted for the acid. These inner jars were also weighed every 24 hours to determine the amount of water absorbed by the salt. Neither method showed a marked change of weight but noticeable differences were found when the inner jars contained calcium chloride and were surrounded by an atmosphere of 100 per cent humidity at 35°C. Gettans<sup>12</sup> has measured the penetrability of varnish films in the same manner for the purpose of evaluating coating materials used for the protection of works of art. This worker found alkyd resins quite impermeable and satisfactory for such purposes.

Grün<sup>13</sup> has also made determinations employing a permeable disc, covered with the protective coating, subjected to the action of water at elevated pressures. Wray and Van Vorst<sup>14</sup> have studied three different methods for determining the penetration of moisture through paint films and compared the results obtained. The most valuable information was obtained by measuring the permeability of the coatings individually. This was done by stretching the films across the tops of Petri dishes which had been partially filled with activated alumina. The Forest Products Laboratory method which was also used consisted of applying various paints and varnishes to selected panels of yellow birch 4 by 8 by 5/8 inches which, after drying, were weighed and placed in an atmosphere of 95 per cent humidity at 77°C. for two weeks, when any increase in weight was noted. The third procedure tested employed circular panels of coated wood, 5.3 cm. in diameter, which were fastened to the tops of jars in the same manner as if the film alone was used as a medium of separation between the two atmospheres. Edwards<sup>15</sup> has written a discussion of the results of Wray and Van Vorst in an attempt to interpret moisture permeability measurements. He stated that there are many advantages in determining moisture permeabilities of paints by films alone and then, with the results from this work at hand, the more complex phenomena observed with films on wood may be interpreted.

Morrell<sup>16</sup> has discussed the factors affecting the absorption of water by varnish films. He has suggested that it is a function of the composition, manner of drying and aging of the film. Absorption is retarded by the presence of salts in the water, even in small amounts, as the difference in effect of tap and distilled water may be detected. After drying, the film will show a larger absorption value upon repeated treatment. Alternate exposure to air and water appears to reduce the amount of absorption, due to oxidation and polymerization. An elastic water-resisting varnish showed 0.3 per cent absorption in 1 day, 0.4 per cent in 2 days, 1.9 per cent in 5 days and 2.8 per cent in 9 days, and at the end of this period still remained clear. Varnishes with low water-absorption show, however, a tendency to bloom if the superficial drying of the film is pronounced.

Wilkinson and Figg<sup>17</sup> have determined the absorption of varnish films when prepared on aluminum sheets. The coated plates were suspended in a hot water bath and after the required time had passed they were removed, dried carefully

<sup>12</sup> J. Gettans, *Tech. Studies Field Fine Arts*, 1932, 1, 63; *Chem. Abs.*, 1933, 27, 433.

<sup>13</sup> R. Grün, *Tonind Ztg.*, 1932, 56, 1087; *Chem. Abs.*, 1933, 27, 1525.

<sup>14</sup> R. I. Wray and A. R. Van Vorst, *Ind. Eng. Chem.*, 1933, 25, 842.

<sup>15</sup> J. D. Edwards, *Ind. Eng. Chem.*, 1933, 25, 846.

<sup>16</sup> R. S. Morrell, "Varnishes and Their Components," H. Frowde and Hodder & Stoughton, London, 1923.

<sup>17</sup> J. A. F. Wilkinson and E. F. Figg, *J. Oil, Colour Chem. Assoc.*, 1924, 7, 232; *Chem. Abs.*, 1925, 19, 1954.



and weighed. It was found that the thin films absorbed a greater amount of moisture than the thicker ones when calculations were based on the percentage of weight increase. The absorption was found to be the same, however, irrespective of thickness of film, when the result was based on quantity of moisture per unit area, provided the films were newly prepared. Absorption increases with the temperature and is approximately twice as rapid at 40°C. as it is at 20°C. Measurement of the thickness of the films showed that the volume of the film increased by an amount equal to the quantity of the water absorbed. It may be pointed out that the curves showing the progress of this action are parabolic, and that absorption will therefore theoretically proceed indefinitely; practically, however, the distended varnish cells will eventually rupture, thus destroying the coating.

Jaeger<sup>57</sup> has studied the porosity of films. The surface to be varnished was coated, first, with a metallic salt and, after it dried, a coat of varnish applied. When the finish dried the upper surface was treated with an aqueous solution of a reagent which gave an intense color reaction with the metallic salt under the protective coating. In this way minute pores can readily be detected in transparent films on opaque surfaces. In a similar fashion opaque films can be investigated by using a transparent base such as glass. Oil varnishes were shown to be distinctly porous. This test is of assistance in interpreting results obtained on the permeability of films by other methods.

#### VARNISHES AS PROTECTIVE COATINGS

No attempt will be made in this section to give a comprehensive outline of the various applications of varnishes in which they are used as protective coatings. On the contrary, only a few of the special uses will be mentioned. The testing of coatings intended for such purposes can be carried out by means of the several methods already described in this chapter and in addition various investigators have outlined and employed special tests for the coatings in which they have been particularly interested. For example, the tests which have been used for electrical refrigeration coatings have been outlined.<sup>58</sup> These include examinations for water resistance, flexibility, adhesion, grease resistance, resistance to yellowing, mar resistance and opacity of the paint or varnish film. Tests would seem to indicate that synthetic resins used in protective coatings offer the advantages of faster and better drying and also greater durability.

#### APPLICATIONS FOR PIPE AND TANK PROTECTION

Gardner<sup>59</sup> has pointed out the results of research in which a semitransparent coating for pipes was sought. It was found that raw oil paint dried too slowly, but that the durability was high although oleoresinous varnishes had poor durability if the oil content was low. Pigmentation and a high percentage of tung oil contributed to the durability but at an increased cost. For heat-treated oils certain mixtures of drying oils gave good results, especially when combined with highly dispersed zinc chromate. Synthetic resins were highly durable and resistant. Asphalt varnishes failed when exposed to the sun and nitrocellulose compositions involved a fire hazard but had many mechanical advantages. Kimpflin<sup>60</sup> has discussed the various applications of synthetic resins to pipe and oil tank coatings. It was found that paints made from synthetic resins were satisfactory for protect-

<sup>57</sup> P. Jaeger, *Farben Ztg.*, 1924, 29, 507; *J.S.C.I.*, 1924, 43, 303B.

<sup>58</sup> D. G. Darroch, *Chem. Eng. Mining Rev.*, 1932, 25, 60; *Chem. Abs.*, 1932, 27, 613.

<sup>59</sup> H. A. Gardner, *Chem. Met. Eng.*, 1931, 38, 402.

<sup>60</sup> G. Kimpflin, *Peintures, pigments, vernis*, 1931, 8, 1606, 1629; *Chem. Abs.*, 1932, 26, 1139. *Inst. Metals*, 1925, 32, 551; *Chem. Abs.*, 1925, 19, 1932.

ing crude oil tanks both ashore and in tankers whereas other materials so far on the market were quite unsatisfactory. This worker also stated that phenol synthetic resin finishes will protect water pipes against the action of chlorine.

Gill<sup>61</sup> has given a discussion of the general status of pipe line protection. It was stated that the impermeability of coatings depends upon their resistance to deterioration from chemical and bacterial action, the freedom from capillary pores and the resistance to mechanical distortion. The latter of these conditions is considered the most important.

#### FINISHES AS AIRPLANE COATINGS

Whitmore<sup>62</sup> has outlined the properties which a good coating should have for airplane service. These requirements are high resistance to water-permeability, the use of pigments which tend to passivate metals and prevent corrosion, the absence of pigments of alkaline reaction, good adhesion to metals which may not be chemically clean and high resistance to impact and bending even after exposure. McCloud<sup>63</sup> has also listed the requirements of such coatings. It was stated that they should have good appearance and adhesion and also prevent the corrosion of light metal alloys. These coatings were evaluated according to the change in tensile strength and percentage of elongation as exhibited by coated test bars of various metals after exposure. Results of such tests of various coatings with particular reference to variations in the priming coat on duralumin, magnesium alloys and steel, showed a zinc chromate-synthetic resin primer to exhibit desirable characteristics. This first coat with an aluminum lacquer top coat gave outstanding protection. Edwards and Wray<sup>64</sup> have discussed the protection of aluminum by means of coatings. For certain purposes the yellowing of an ordinary varnish makes its use questionable as a transparent finish. Some of the newer synthetic resin varnishes, as, for example, those of the glycerol phthalate type, showed very satisfactory results over a substantial period. This group was shown to possess even greater durability than cellulose lacquers, and the adhesion to aluminum surfaces was excellent. Certain of the vinyl resins also gave satisfactory performance.

#### RESISTANCE OF COATINGS TO DISCOLORATION

Van Heuckeroth<sup>65</sup> has observed the yellowing of a large number of lacquers made using resin bases. Films of the lacquers were prepared in the same manner as for tensile strength tests and strips of the films were enclosed in cardboard folders so that a circle of the film 2 cm. in diameter was exposed while the balance of the piece was protected. Films were subjected to radiation from quartz lamps for two hours while the cabinet was maintained at a temperature of 70°C. The change in color of the films was determined by means of a varnish colorimeter.<sup>66</sup> He noted that many resins showed a tendency to blacken instead of yellow and also that plasticizers of the phthalate type exhibited but slight yellowing.<sup>67</sup>

<sup>61</sup> S. Gill, *Ind. Eng. Chem.*, 1933, 25, 49.

<sup>62</sup> M. R. Whitmore, *Ind. Eng. Chem.*, 1933, 25, 19.

<sup>63</sup> J. L. McCloud, *Ind. Eng. Chem.*, 1931, 23, 1334.

<sup>64</sup> J. D. Edwards and R. I. Wray, *Ind. Eng. Chem.*, 1933, 25, 23.

<sup>65</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 369.

<sup>66</sup> A. W. Van Heuckeroth, *Circ., Am. Paint, Varnish Mfrs. Assoc.*, 1930, 367.

<sup>67</sup> As to the possibility of decreasing the yellowing tendency of varnishes using synthetic resins, B. Peters (British P. 295,941, Aug. 8, 1928; *Chem. Abs.*, 1929, 23, 924) has stated that by addition of a small proportion, about 0.5%, of a strong organic or inorganic acid, acidic salt or nitrate soluble in the varnish, the fastness to light can be greatly increased. Suitable substances include trichloroacetic, perchloric, hydrochloric, sulphuric, nitric and nitrous acids, aluminum, ferric and cupric chlorides, bisulphates and the nitrates of calcium, bismuth, thorium, uranium and cobalt.

D. C. Duncan, W. P. Davey and D. R. Wiggam (*Ind. Eng. Chem.*, 1931, 23, 904.) have investigated the coloring of lacquer films under the action of ultraviolet light.

**Appendix**  
**Trade Names List**

## Trade Names List

Synthetic resins are known and sold commercially under various trade names which to the uninitiated give little clue as to their chemical nature and uses. The accompanying compilation lists the trade names of synthetic resins and plastic materials, showing wherever possible their chemical type. Included in the list are the names of fabricated resin products as well as those of the original molding, casting and coating compositions. Related products, such as cellulose, casein, asphalt and natural resin compositions, are also represented in part—especially if the materials are well known or the name is similar to that of a synthetic resin composition.

The trade names, arranged alphabetically,<sup>1</sup> are followed in turn by abbreviations designating the chemical type or composition (e.g., phenol-formaldehyde resin); the form and use (such as soluble varnish resin, molding composition); the manufacturer or distributor, with addresses; and references giving the source of the information.<sup>2</sup>

### ABBREVIATIONS

#### Composition

B	Inorganic
C	Casein
CA	Cellulose acetate
D	Resin used as ingredient
F	Fabricator's trade name
GP	Glycerol-phthalic anhydride
PF	Phenol-formaldehyde
Px	Pyroxylin
RPG	Rosin-phthalic anhydride-glycerol
SR	Synthetic resin
UF	Urea-formaldehyde
V	Viscose
W	Wood fiber
X	Miscellaneous
?	Nature not known

#### Forms, Uses

f	Sheets, rods, tubes
l	Laminated
m	Molding composition
s	Soluble type (for coatings and impregnation)
t	Turnery type (cast and machined articles)
SG	Safety glass
P	Packaging material

<sup>1</sup> Initials are filed under first letter without regard for "and," periods or hyphens. Compound names, with or without hyphen, are indexed under first name.

<sup>2</sup> Some of the items in the list have been obtained from the advertising pages of the references given. Where no source is indicated, the information has been ascertained from trade announcements and catalogs or by private communication.

## Sources

APV-1	<i>American Paint &amp; Varnish Mfrs. Assn. Scientific Section Educational Bureau, Circular 369, "Physical Properties of Synthetic Resins in Lacquers," 1930.</i>
APV-2	Same, No. 429. "Lacquer Liquids," 1933.
APV-3	Same, No. 430. "Synthetic Resin Index," 1933.
AR	"Artificial Resins," by J. Scheiber and K. Sändig, Translated by E. Fyleman; Pitman & Sons, Ltd., London, 1931.
BP	<i>British Plastics and Moulded Products Trader</i> ; Plastics Press Ltd., London.
BPY	"British Plastics Year Book, 1933," Plastics Press, Ltd., London.
Ce	<i>Cellulose</i> ; Cellulose Publishing Co., New York.
CGP	<i>Le Caoutchouc et la Gutta-Percha</i> , Paris.
CM-1	<i>Chemical and Metallurgical Engineering</i> , 1931, <b>38</b> , 461.
CM-2	<i>Chemical and Metallurgical Engineering</i> , 1932, <b>39</b> , 523.
CM-3	<i>Chemical and Metallurgical Engineering</i> , 1933, <b>40</b> , 483.
CM-4	<i>Chemical and Metallurgical Engineering</i> , 1934, <b>41</b> , 589.
GZ	<i>Gummi-Zeitung</i> , Berlin.
H	"Plastics and Molded Electrical Insulation" by E. Hemming; Chemical Catalog Co., New York, 1923.
J	"Chemische Technologie der Lösungsmittel" by O. Jordan; Julius Springer, Berlin, 1932.
K-1	<i>Kunststoffe</i> , 1925, <b>15</b> , 116.
K-2	<i>Kunststoffe</i> , 1932, <b>22</b> , 207.
K-3	<i>Kunststoffe</i> , 1932, <b>22</b> , 222.
K-4	<i>Kunststoffe</i> , 1932, <b>22</b> , 254.
K-5	<i>Kunststoffe</i> , 1933, <b>23</b> , 37.
K-6	<i>Kunststoffe</i> , 1933, <b>23</b> , 107; 1935, <b>25</b> , 37.
KPM	"Handbuch der künstlichen plastischen Massen" by O. Kausch; J. F. Lehman, München, 1931.
Kunst.	<i>Kunststoffe</i> , J. F. Lehman, München.
Nitro.	<i>Nitrocellulose</i> , Verlag Panesgrau, Berlin-Wilmersdorf.
NSR	"The Chemistry of the Natural and Synthetic Resins" by T. H. Barry, A. A. Drummond and R. S. Morrell; D. Van Nostrand Co., New York, 1926.
OPD	<i>Oil, Paint and Drug Reporter</i> .
PGB-1	"Plastics Directory and Buyer's Guide, 1928"; Hoffman Publications, Inc., New York.
PGB-2	"Plastics Directory, Index and Buyer's Guide, 1929"; Plastics Publications, Inc., New York.
PGB-3	"Plastics Guide Book, 1934"; Plastics Publications, Inc., New York.
Plastics	Plastics, Plastics and Molded Products, Plastic Products; Plastics Publications, Inc., New York. Modern Plastics; Breskin & Charlton Publishing Corp., New York.
PM	"Plastische Massen" by H. Blücher; Salomon Hirzel, Leipzig, 1924.
RGP	<i>Revue generale des matieres plastiques</i> , Paris.
S	"Sicherheitsglas" by Bodenbender; Bodenbender, Berlin-Steglitz.
Syn. Appl. Fin.	<i>Synthetic and Applied Finishes</i> .

It will be noted in the source column that certain references are composed of a letter or letters joined to a number by a hyphen. These indicate a specific source that is fully given in the key. References to books are given by a group of letters (defined in the key) followed immediately (without a hyphen) by the page number. Thus, APV-1 indicates that the source of the material is American Paint & Varnish Mfrs. Assn. Circular 369; whereas KPM278 designates Page 278 of Kausch's "Handbuch der künstlichen plastischen Massen."

Name	Composition	Forms, Uses	Company	Source
<b>A-K</b>	PF	m, asbestos filler	K. Albert G. m. b. H., Amöneburg, Germany	CGP, 1932, 20 15954; CM-4
<b>A.F.S.</b>	Aniline, formaldehyde and sulphur	Substitute for Canada balsam		<i>Chem. Abs.</i> , 1931, 25, 1858.
<b>A-W 2</b>	SR		I. G. Farbenind. A.-G. Germany	CM-4
<b>Abalak</b> (Abalack)	PF	s	Kunstharzfabrik Dr. F. Pollak, Vienna	APV-2; CM-4; NSR118
<b>Abalyn</b>	Methyl esters of abietic acid	Plasticizer for nitrocellulose lacquers	Hercules Powder Co., Wilmington, Del.	APV-3; CM-4
<b>Abrac</b>	Rosin glyceride			NSR149
<b>Abracol</b>	Toluene-sulphonic acid esters	Plasticizer	A. Boake, Roberts & Co., England	APV-2; J293
<b>Ace-Itc</b> (Aceite)	Bituminous composition		American Hard Rubber Co., Akron, O.	APV-2; CM-4, PGB-3
<b>Acelloid</b>	CA	m	General Plastics Corp., Ltd., London, S.E. 13	CM-4; <i>Plastics</i> , 1933, 8, 466
<b>Aceloid</b> (Aceloide)	CA		Cie Petit-Collin-Oyonnithé, Paris, France	PGB-2; CM-4
<b>Acelose</b>	CA		American Cellulose Co. Indianapolis, Ind.	CM-4, PGB-2
<b>Acéta</b>	CA		Cie. Petit-Collin-Oyonnithé, Paris	CM-4, APV-2
<b>Acetaloid</b> (Aceteloid)	CA	f, m	Acetate Products Corp., Ltd., London, E.C. 4	BPY; CM-4
<b>Acetoid</b>	CA		Punfield & Barstow, Ltd., London	APV-2, CM-4
<b>Acetol</b>	CA	Flake	Soc. Usines Rhone-Poulenc, Paris	APV-2; CM-4
<b>Acetyloid</b>	CA		Dai-Nippon Celluloid Co., Ltd., Sakai, Japan	BPY, CM-4
<b>Acetylon</b>	CA		Dynamit A.-G. vorm. A. Nobel, Hamburg	APV-2, CM-4
<b>Acidur</b>		Acid-resistant moldings	Cable Mfg. Co., Ltd., England; Bratislava, Czechoslovakia	CM-4
<b>Acrollite</b>	Phenol-glycerol	m, l	Continental-Diamond Fibre Co., Newark, Del.	CM-4, AR194
<b>Adit</b>		m	Gehr. Adt A.-G., Wächtersbach, Germany	CM-4
<b>Aerialite</b>	SR		S. Alcock & Co., Ltd., England	K-2; CM-4
<b>Aeternol</b>	SR		I. G. Farbenind. A.-G., Frankfurt, Germany	OPD, 1934, 126 (16), 19.
<b>Aeyollit, see</b> <b>Haefelyte</b>				CM-4
<b>Agalyn</b>	Px	Dentures	J. D. Whyte, Pittsburgh	CM-4
<b>Agatine</b>	PF	t, f	Soc. Nobel Francaise, London, E.C. 1	CM-4
<b>Age-rite Resin</b>	Aldonaphthylamine			<i>Chem. Met. Eng.</i> , 1928, 26, 622
<b>Aleo</b>		Cold molding	American Insulator Corp., New Freedom, Pa.	CM-4
<b>Akalit,</b> (Akalith, Akelit)	C		Akalit Kunsthornwerke A.-G., Vienna	CM-4
<b>Aleo Resin, Hard, Extra Hard</b>	Natural resin and PF	4-hour varnish	American Cyanamid & Chemical Co., New York	APV-3

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Name	Composition	Forms, Uses	Company	Source
<b>Akrol</b>	Glycerol resin		U.S.S.R.	CM-4
<b>Aladinite</b>	C	f	Aladinite Co., Inc., Orange, N. J.	CM-4
<b>Alastik</b>	PF		Atas Ago Chem. Fabrik A.-G., Leipsig, Ger.	K-2
<b>Albane</b>		Plastics	Soc. Rhodiaseta, Paris	CM-4
<b>Albertit</b>	PF	t, f	Scott, Bader & Co., Ltd., London, W C. 2, Chem. Fabr. Dr. Kurt Albert, Wiesbaden, Germany	CM-4; BPY
<b>Albertat</b>	Al salt of Alber- tol, q v			CM-4
<b>Albertol</b>	PF, F	Modified, s	Scott Bader & Co., Ltd., Lon- don, W C 2; Röhm & Haas Co., Philadelphia; Chem. Fabriken Dr. Kurt Albert, Wiesbaden, Germany	CM-4, BPY, AR270
<b>Abollit</b>	PF	t	Augsburger Kunsthartz-Fabrik, Augsburg, Germany	CM-4
<b>Alboresin</b>	UF	m	Kontakt-Römmler A.-G., Frank- furt, Germany	CM-4
<b>Alcolite</b>	Px	Denture	Alcolite, Inc., Philadelphia	CM-4
<b>Aldur</b>	UF	m, t	Inco Products Corp., Brooklyn, N. Y.	CM-4; <i>Ind. Eng Chem.</i> , 1928, <b>20</b> , 1367
<b>Aldydale</b>	PF	Blocks, molded articles	I. G. Farbenind. A.-G., Frank- furt, Germany	K-2, CM-4
<b>Alfordor</b>	SR	Shelves	Alford & Alder, Ltd., London, England	BP, 1934, <b>6</b> , 86
<b>Alftalat</b>	Alkyd resin		Chem. Fab. Dr. Kurt Albert, Wiesbaden, Germany	APV-2; CM-4
<b>Algolith</b>	Algine plastic		De Charrard, Rueil, France	PGB-2; CM-4; K-1
<b>Algine</b>	Sea-weed- celluloid	Molding comp.	Paul Glaess, Paris	K-2; CM-4, KPM271
<b>Alkalit</b>	Sodium salt of phenolphthalein condensed with toluoyl chloride	Coatings		CM-4; <i>Chem. Abs.</i> , 1932, <b>26</b> , 5220
<b>Alkalit</b>	C		Alkalit Kuntsthornwerke A.-G., Vienna	CM-4
<b>Alkolite</b>	Phenolphthalein resin			APV-2
<b>Alkydal T, TT, ST</b>	Phthalic glyceride	s	I. G. Farbenind. A.-G., Frank- furt, Germany	J88
<b>Alloprene</b>	Chlorinated rubber		Imperial Chem. Industries, Ltd., London S.W. 1	<i>Syn. App. Fin.</i> 1934, <b>5</b> , 135
<b>Alloy C</b>	?, SR		William Jessop & Sons, Ltd., Sheffield, England	KPM271; CM-4
<b>Alvar</b>	Polyvinyl acetate-acetal	Coatings and plastics	Shawinigan Chemicals, Ltd., Montreal; Shawinigan Products Corp., New York	CM-4; APV-3
<b>Amalith</b>	PF			KPM271; CM-4; AR337
<b>Amberdeen</b>	PF			NSR118; CM-4; KPM271
<b>Amberglow</b>	PF	t, luminous	Laboratoires Industriels d'Asnières, Paris	CM-4
<b>Amberit (Amberite)</b>	PF	s	U. S. A.	NSR118; CM-4 KPM271,
<b>Amberlac</b>	SR		Resinous Products & Chemical Co., Philadelphia	OPD, 1934, <b>126</b> (18), 21

Name	Composition	Forms, Uses	Company	Source
<b>Amberlite</b>	SR		Resinous Products & Chemical Co., Philadelphia	OPD, 1934, 126 (18), 21
<b>Amberol</b>	PF	s	Resinous Products & Chemical Co., Philadelphia	APV-2, 3; CM-4
<b>Ambloid</b>	C		Dai-Nippon Celluloid Co., Ltd., Sakai, Japan	CM-4; BPY
<b>Ambra</b>	PF	t, clear solid		CM-4; <i>Plastics</i> , 1928, 4, 263
<b>Ambrasit</b>	PF	t	Chemische Fabrik Ambrasit, Vienna, H. Illner, London, E.C.1	CM-4; BPY
<b>Ambroid</b>	Pressed amber			PM188; CM-4
<b>Ambroin</b>	PF, etc.		Ver. Isolatorenwerke A.-G., Vienna	CM-4; KPM271
<b>Ambroine</b> , also called <b>Stabilite</b>	X, copal-fiber	f	Soc. Grandgener, Perreux, France	CM-4; <i>Plastics</i> , 1928, 2, 123
<b>Ambrol</b>	SR	s		NSR136; PM216
<b>Amerline</b>		Insulators	American Insulator Corp., New Freedom, Pa.	PGB-1; CM-4
<b>Amerith</b>	Px	f	Celluloid Corp., Newark, N. J.	PGB-1; CM-4
<b>Amerloid</b>	F		Amerloid Mfg. Co., Brooklyn, N. Y.	PGB-3; CM-4
<b>Ameroid</b>	C		American Plastics Corp., New York	K-5
<b>Amiantine</b> (Amianthine)	PF?, copal plastic		Soc. Roux, Paris	KPM271; CM-4
<b>Aminoplast</b>	UF	General name for the hardened condensation product of ureas with aldehydes. Corresponds to "Phenoplast" and "Resite"		<i>Kolloid-Z.</i> 1927, 42, 175; AR160
<b>Anka</b>	D	Insulating parts	Callenders Cable & Construction Co., London, England	BP, 1934, 6, 40
<b>Annealocic</b>	Bitumen, etc	Insulating materials	Telegraph Const. & Maintenance Co., London, E.C. 3	CM-4
<b>Aqualac</b>	Shellac		Kasebier Chatfield Shellac Co., New York	PGB-1
<b>Aqualite</b>	PF	l	National Vulcanized Fibre Co., Wilmington, Del.	
<b>Aquaresin GM</b>	Glycol boriborate		Glyco Products Co., Inc., Brooklyn, N. Y.	CM-4
<b>Arbolite</b> , (Arbolite B)	F?	f, l	N. V. Philips's Gloeilampenfabrieken, Eindhoven, Holland; Philips Industrial "Raw Materials" Dept., London, W.C. 2	BPY
<b>Arcolite</b>	PF, F	m	American Record Corp., Scranton, Pa.	PGB-3, CM-4
<b>Ardasell</b>	?	Cement	Syments Products, Ltd., Eccles, Lancs., England	BPY
<b>Ardenite</b>	PF?	m	F. G. Stokes, Ltd., Altrincham, England	CM-4
<b>Argolit</b>	C		Argo Chem. & Nahrungsmittel Fabrik, Prerov, Czechoslovakia	PGB-1; CM-4
<b>Aroclor</b>	Chlorinated biphenyl resins	Compatible with nitrocellulose	Swann Chemical Co., Anniston, Ala.	APV-3; CM-4 OPD, 1934, 126 (23), 35
<b>Asbedex</b>	Asbestos composition		Dixie, Ltd., London	<i>Plastics</i> , 1929, 5, 187



Name	Composition	Forms, Uses	Company	Source
<b>Ashdown</b>	PF, etc	m	H. E. Ashdown (Birmingham), Ltd., Birmingham, England	BPY
<b>Askol</b>	PF		Anglo-Scottish Chemical Co., Ltd., Glasgow, Scotland	CM-4
<b>Astrinite</b>	Bitumen plastic	Acid- and alkali-proof molding	General Plastics Corp., Ltd., London, S E 13	<i>Plastics</i> , 1932, 8, 39; CM-4
<b>Astro-Kopal</b>	?SR, contains rosin			<i>Farben-Ztg.</i> , 1930, 32, 1981
<b>Athrombit</b>	Px, F		F. u M. Lautenschlager, Munich, Germany	K-2; CM-4
<b>Atlas</b>	PF	l	H. Clarke & Co (Manchester), Ltd., Manchester, England	K-6; CM-4
<b>Ausco</b>			Carl Austin & Co., Ltd., Toronto	PGB-1
<b>Australite</b>				PGB-2; CM-4; K-1
<b>Aveco</b>	? Leatheroid		Willmott, Son & Phillips, Ltd., London, E C 3	BPY
<b>Avecolite</b>	PF	l	Willmott, Son & Phillips., Ltd., London, E C 3	CM-4
<b>BCM/Brownie</b>	SR?	m, f	Brownie Wireless Co. (Great Britain), Ltd., London, N.W 1	CM-4; BPY
<b>"BkL" Laminated</b>	PF, Plywood base	l	Bousefields, Ltd., London	BP, 1934, 6, 7
<b>B.T.H.</b>	?	m, l, f	British Thomson-Houston Co., Ltd., Rugby, England	BPY
<b>Bakdura</b>	PF			<i>Plastics</i> , 1930, 6, 705; CM-4
<b>Bakelaque</b>	PF	l, s	Attwater & Sons, Preston, England, Mica & Insulating Supplies Co., Melbourne, Victoria, Australia	CM-4; BPY
<b>Bakelite (Bakelit)</b>	PF	m, l, s, t	Bakelite Corp., New York, N. Y., Bakelite, Ltd., London, S.W. 1; Bakelite G.m.b.H. Berlin, Ger	CM-4; APV-3; KPM 272; BPY
<b>Balance</b>		Molded insulation	Belden Mfg. Co., Chicago	PGB-1
<b>Balenit</b>	Shellac base			K-1; CM-4; <i>Kunst.</i> , 1920, 10, 110
<b>Bandalasta</b>	UF, F		Brookes & Adams, Ltd., Birmingham, England	CM-4
<b>Barber and Duffy</b>	PF	m	Barber & Duffy, Leeds, Yorks., England	K-6
<b>Barnacle</b>	?	m, f	E. W. Puckert, Ltd., West Croydon, England	BPY
<b>Baykofaden</b>			Farbenfabriken Fr. Bayer, Leverkusen, Germany	PGB-2
<b>Beacon</b>	UF, F	Ware		CM-4
<b>Beatl, see Beetle</b>	UF	Ware	Beatl Sales, Ltd., England	CM-4
<b>Beatiware, M-L. See M-L Beatiware</b>				
<b>Behrit</b>		m		<i>Kunst.</i> , 1932, 23, 245; CM-4
<b>Beck-O-Lac</b>	SR		Beck, Koller & Co., Inc., Detroit, Mich.	APV-2; CM-4
<b>Beckacite</b>	PF or alkyd resin	Varnishes and lacquers	Beck, Koller & Co., Inc., Detroit, Mich.; A. F. Suter & Co., Ltd., London, E.C.	APV-3; CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Beckkolloid</b>	SR	Plastics	Beck, Koller & Co., Inc., Detroit, Mich.	O.P.D., 1934, 126 (27), 54
<b>Beckosol</b>	SR		Beck, Koller & Co., Inc., Detroit, Mich.	CM-4
<b>Beetle</b>	UF	m	Synthetic Plastics Co., New York; Beetle Products Co., Ltd., London, W.1	CM-4
<b>Beetleware</b>	UF, F		Beetleware Corp., New York	CM-4
<b>Belco</b>	Cellulose		Nobel Chemical Finishes, Ltd., Slough, Bucks., England	KPM-272; CM-4
<b>Bell</b>		Molding	Northern Industrial Chem. Co., Boston, Mass.	PGB-1
<b>Belleroid</b>	Rubber base		Barret & Elers, Ltd., London, E 3	CM-4
<b>Belling-Lee</b>	C & SR, F	f	Belling & Lee, Ltd., Enfield, Middlesex, England	BPY; CM-4
<b>Belplastic</b>	F	Ware	Belplastic, Ltd., London, W 10	CM 4
<b>Bennetate</b>	CA		B. A. Parker, London	APV-2; CM-4
<b>Benzex</b>	Benzyl cellulose		British Xylonite Co., Ltd., London, E 4	BP, 1933, 4, 423
<b>Bernit</b> (Bernite)	CA		Zelluloidwaren Fabrik., Zollikofen, Switz.	APV-2; CM-4
<b>Beutene</b>	Amline-butyraldehyde		Naugatuck Chemical Co., Naugatuck, Conn.	CM-4
<b>BeX</b>	PF, etc., F		British Xylonite Co., Ltd., London, E 4	CM-4
<b>Bexite</b>	PF, etc.	f	British Xylonite Co., Ltd., London, E. 4	BPY; CM-4
<b>Bexoid</b>	CA		British Xylonite Co., Ltd., London, E 4	APV-2; CM-4
<b>Bikarton</b>	PF	l		Plastics, 1930, 6, 705; AR355; CM-4
<b>Bimollithe</b>	Resorcinol and trioxymethylene		German General Electric Co., Berlin	APV-2
<b>Bincollite</b> (Bincollithe)	Resorcinol and trioxymethylene	m	Allgemeine Elektrizitäts-Ges A.-G., Berlin	PGB-2, CM-4; K-2
<b>Birmite</b>	UF, F		E. Elhott, Birmingham, England	CM-4
<b>Bitose</b>	Refined asphalt or bitumen		Grinwood & De Geus, Ltd., London, E C 2	BPY
<b>Bituba</b>	PF	l		Plastics, 1930, 6, 705; CM-4; AR355
<b>Bonnyware</b>	F, UF, PF	Ware	Reynolds Spring Co., Jackson, Mich.	Plastics, 1932, 8, 285; CM-4
<b>Book End</b>	SR	Moldings	Kuhn & Jacob Molding Co., Trenton, N. J.	K-6; CM-4
<b>Boschbakelit</b> (Bosch Bakelite)	PF		Robert Bosch, Stuttgart, Germany	Plastics, 1930, 6, 705; AR347; CM-4
<b>Braylite</b>	W, binder		American Insulator Co., New Freedom, Pa.	CM-4; Plastics, 1933, 8, 466
<b>Bresin</b>	SR		Hercules Powder Co., Wilmington, Del.	CM-4
<b>Britmac</b>	C, PF, F		C. H. Parsons, Ltd., Birmingham, England	CM-4
<b>Britsultite</b>	PF	m	British Insulite, Ltd., Rochdale, England	CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Brofo</b>	Cumarone resin		Brown & Forth, Ltd., London, N.W. 1	APV-2; CM-4
<b>Brolonkapseln</b>	Cellulose capsules		Chemische Fabrik von Heyden A.-G., Germany	CM-4; KPM273
<b>Brownie</b>	SR	m	Brownie Wireless Co (Great Britain), Ltd.; London, N W. 1	BPY
<b>Bucheronlum</b>	PF	Shellac subat	Köln-Ehrenfeld, Germany	NSR118, 124; AR283
<b>Buffalo</b>		Moldings	De Jur Products Co., New York	PGB-1
<b>C-E 950</b>	PF	Dentures	Coe Laboratories, Inc., Chicago	CM-4
<b>C. F. Board</b>	PF	l	Campbell Fibre Co., Stanton, Del	CM-4
<b>Cabtyrit</b>	?	Acid-resisting industrial linings	St. Helen's Cable & Rubber Co., Ltd., Slough, Bucks, England	BPY
<b>Campbellite</b>	PF	l	Campbell Fibre Co., Stanton, Del.	CM-4
<b>Campico</b>			Campbell Fibre Co., Stanton, Del.	PGB-1
<b>Camphrosal</b>	p-Toluenesulphonamide		Chem. Fabrik von Hayden, Germany	J253, 320
<b>Carben</b>	Acetylene condensation products (Cuprene)		Elektrizitätswerke Lonza, Basle, Switzerland	KPM273
<b>Carbolite</b> (Carbolithe)	PF	m	Soc gen des Matières Plastiques, France	CM-4; K-2
<b>Carbolithe</b>	SR		Soc. Française, Lyons, France	PGB-1
<b>Carboloid</b>	PF	m	Carboloid Products Corp., New York Dai-Nippon Celluloid Co., Ltd., Sakai, Japan	CM-4; BPY
<b>Carbonex</b>	Coal-tar pitch	Softener for rubber	Barrett Co., New York	
<b>Cardollite</b>	Cashew oil polymer		Irvington Varnish & Insulator Irvington, N. J.	Du Pont <i>Du Prene Manual</i> , p. 42
<b>Carnallithe</b>	C		Barthelemy, France	PGB-2
<b>Carnoid</b>	C		Cie Général d'Electricité, France	K-1; PGB-2
<b>Carta</b>	PF	l	Isola-Werke A.-G., Düren, Germany	CM-4
<b>Casolith</b>	C		Hollandsche Casolith-Werke, L. M. Meers, London E.C. 1. Soc Oyannithe, Montville, Rouen, France	CM-4; PGB-2
<b>Cassold</b> (Cassoide)	C		Maison Blanpain, Esy, France	K-1; PGB-2
<b>Catalazuli</b>	PF	t	Catalazuli Manufacturing Co., College Point, L. I., N. Y.	CM-4; PGB-3
<b>Catalin</b>	PF	s, t	American Catalin Corp., New York	APV-2; CM-4; KPM273
<b>Cégélite</b> (Cegelite) (Cegelite)	PF	m	Cie. Général d'Electricité, Paris; Manufacture d'Isolants & Objets Moules, Vitry, France	APV-2; BPY
<b>Cel-O-Glass</b>	CA	Coated netting	Acetol Products, Inc., New York	CM-2
<b>Celanese</b>	CA		Celanese Corp., New York	CM-4
<b>Celastie</b>	Px	Box toe material	Celastie Corp., Arlington, N. J.	CM-4
<b>Celastoid</b>	CA	f	British Celanese, Ltd., London, W. 1	BPY; CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Celerit</b>		Modeling composition	Apotela, Ltd, Zurich	CM-4
<b>Celoron</b> See Celoron				
<b>Celescot</b>	Px	m	Celescot Co., Toledo, Ohio	PGB-2; CM-4
<b>Celestol</b>	Alkyd Resin		F. A. Hughes & Co, Ltd., London, W. 1	CM-4
<b>Cellanite</b>	Aniline resin ppt. on fibers in paper machine		Continental-Diamond Fibre Co, Newark, Del.	<i>Plastics</i> , 1932, 8, 195; BP, 1932, 4, 286
<b>Cellanite</b>		Laminated board	Micanite & Insulators Co, London, E. 17	CM-4
<b>Cellastine</b>	CA	m	British Celanese, Ltd., London, W. 1	BPY, CM-4
<b>Cellesta</b>	Px		Verein fur Chemische Industrie A.-G., Frankfurt, Germany	PGB-2; CM-4
<b>Cellit</b> (Cellit-L) (Cellite)	CA		Farbenfabriken Fr Bayer, Leverkusen, Germany; Williams (Hounslow), Ltd., Hounslow, Middlesex, Eng.	BPY, APV-2; K-2
<b>Cellomold</b>	CA	Injection molding	F. A. Hughes & Co., Ltd, London, N W 1	CM-4
<b>Cellon</b>	CA	f	F. A. Hughes & Co, Ltd., London, N.W. 1; I. G. Farbenind. A.-G., Troisdorf, Ger., Dr. A. Eichengrün, Germany	KPM273; CM-4; K-2; BPY
<b>Cellulak</b>	F		Irvington Varnish & Insulator Co, Irvington, N J	PGB-1
<b>Cellulith</b>	Wood pulp product			K-2
<b>Celluloid</b>	Px		Celluloid Corp, Newark, N J.	CM-4
<b>Celluloid de Socker.</b> See <b>Celluloid Lehmann</b>				CM-4
<b>Celluloid Lehmann</b>	Waxes, starch, casein, etc.			CM-4
<b>Cellulosine</b>	Celluloid bleached by a double salt of Na and Mg sulphite and acid		E. Cadoret and E. Degraide	K-2
<b>Celoron</b>	PF	l, m	Continental-Diamond Fibre Co., Newark, Del; Macechenn & Co., Ltd., London, S.E. 11; Diamond Fibre Co, Ltd, London, S.E. 11	BPY; CM-4
<b>Celtid</b>	Px	f	Rhenisch Gumminannheim-Nockerau, Germany; Adam Bernhard, New York	PGB-1; CM-4
<b>Celvaloid</b>	CA on wood base		Acetate Products Corp., Ltd., London	<i>Plastics</i> , 1929, 5, 157
<b>Cerite</b>	PF	s	Clement & Rivière, Paris	CM-4
<b>Cetec Refractory</b>	Ceramic type, cement-asbestos	Cold molding compositions	General Electric Co., Pittsfield, Mass.	CM-4
<b>Cetec, Non-Refractory</b>	Bituminous type, pitch, oil, asbestos	Cold molding compositions	General Electric Co., Pittsfield, Mass.	CM-4
<b>Chatterton's Compound</b>	Gutta percha, tar and pitch	Insulating material	Pomona Rubber Co., Manchester, England; McGill Mfg. Co., Valparaiso, Ind.	BPY; CM-4; PGB-1
<b>Chlorkaukschuk</b>	Chlorinated rubber		I. G. Farbenind. A.-G., Frankfurt, Germany	J85

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Name	Composition	Forms, Uses	Company	Source
<b>Christollit</b>	PF, F		Westfälische Metallwarenfabrik Christophery G m.b.H., Iserlohn, Germany	K-5; CM-4
<b>Chrystalate</b>		Hot molding composition		CM-4, H170
<b>Ciba</b>	UF, aniline resin	m	Soc. Chem. Ind., Basle, Switz., Ciba Co., Inc., New York	CM-4; PG-B2; K-2
<b>Cibanoid</b>	UF	m, s, l	Ciba Co., Inc., New York, Soc. Chem. Ind., Basle, Switz.; Clay- ton Aniline Co., Ltd., Clayton, Manchester, England	CM-4; PGB-3; BP, 1933, 5, 217
<b>Cinerit</b>	X, waterglass, copal and fillers		Petrier, Tissot & Raybaud, Switz	KPM274, CM-4
<b>Ciro</b>	Px	Records	Celluloid Printers, Ltd., England	CM-4
<b>Clar-Apel</b>	CA	P	Du Pont Cellophane Co., Inc., Wilmington, Del.	PGB-3; CM-4
<b>Claritone</b>	?SR	Articles	Ashley Wireless Telephone Co. (1925), Ltd., Liverpool, England	KPM275, CM-4
<b>Clématite</b>	PF			RGP, 2932, 8, 157; CM-2
<b>Clematélite</b>	Gum composi- tion		Soc. Suisse de Clematélite, Swit- zerland	PGB-1; CM-4
<b>Clematite</b>	Asbestos, bitu- minous			K-2; CM-4; Plastics, 1926, 2, 123
<b>Clonalline</b>	Resins		Soc. Résines & Vernis Artificiels, Lyons, France	CM-4
<b>Co-ORal-ite</b>	PF	Denture	Co-ORal Dental Mfg. Co., Santa Monica, Cal.	
<b>Codite</b>		Thermoplastic, vulcanized in- sulating fiber	Continental-Diamond Fibre Co., Newark, Del.	CM-4
<b>Cogebi</b>	PF, F		Cie. Gen. Belge d'Isolants, Bruxelles	CM-4
<b>Colasta</b>	PF, X, sulpho- nated oil	m	Colasta Co., Inc., Hoosick Falls, N. Y.	PGB-3, CM-4
<b>Colbox</b>		Insulating ma- terials	Blackall Bros., Ltd., London, E. 15	CM-4
<b>Collector Micanite</b>	Acetaldehyde resin-mica	l		AR268
<b>Coltrock</b>	PF	Cold-molding comp.	Colt's Patent Firearms Mfg. Co., Hartford, Conn.	CM-4
<b>Coltstone</b>	X	Cold molding	Colt's Patent Firearms Mfg. Co., Hartford, Conn.	CM-4
<b>Compo-Site</b>	F		Compo-Site, Inc., Newark, N. J.	PGB-1; CM-4
<b>Concordia</b>	F, SR	Molded products	Concordia Elect. Safety Lamp Co., Cardiff, Wales	CM-4
<b>Condensit- Cellulac</b>	PF	l		CM-4
<b>Condensite (Condensit)</b>	PF	m	Bakelite Corp., New York; Bakelite, Ltd., London, S W. 1	CM-4
<b>Condensite- Cellulose</b>	Condensite and vulcanised fiber			KPM275; CM-4
<b>Condulatum</b>		Insulation	Mica Insulator Co., New York	PGB-1; CM-4
<b>Condulline</b>		Insulation	Mica Insulator Co., New York	PGB-1; CM-4
<b>Conite</b>		Fiber products	Continental-Diamond Fibre Co., Newark, Del.	PGB-1

Name	Composition	Forms, Uses	Company	Source
<b>Coolicon</b>	F, PF	Electric-light reflectors	Benjamin Electric, Ltd., London, N. 17	BP, 1935, 6, 440
<b>Coralax</b>	PF		Soc. Française, Vitry, France	CM-1
<b>Cornit</b> (Cornite)		m, pressed paper	H. Weidmann, Ltd., St. Gallen, Switz	CM-4, APV-2
<b>Coronal</b>	UF		Soc. l'Ambrolithe, Paris	CM-4
<b>Crabtree</b>	SR	Moldings	J. A. Crabtree & Co., Ltd., Wall-sall, Staffs., England	K-6
<b>Cresophane</b>	PF, etc		Cie. Franc. d'Exploitation des Procédés Plinatus, Paris	CM-4
<b>Cristaloid</b>	PF	t	France	CM-3; S207
<b>Cristalyx</b>	UF		Edgard Israel, France	CM-1
<b>Crommold</b>	SR?	Articles	Cromwells, Ltd., Dudley Port, Staffs., England	BPY; CM-4
<b>Crommold</b>	SR, F	Ware	Cromwells, Ltd., Dudley Port, Staffs., England	CM-1
<b>Cromware</b>	SR, F	Ware	Cromwells, Ltd., Dudley Port, Staffs., England	CM-4
<b>Crystalate</b>	Shellac base, F	m	Crystalate Gramophone Record Mfg. Co., Kent, England	BPY; CM-4
<b>Crystalite</b>	UF		Röhm & Haas Co., Philadelphia	CM-4
<b>Crystalite</b>	UF	m	Crystalite Corp. of America, New York	CM-4
<b>Crystallithe</b>	SR	Transparent	Léon Castany, Paris	CM-4
<b>Crystallite</b>	UF	m		CM-4; <i>Plastics</i> , 1926, 2, 14
<b>Crystalloide</b>	Px			KPM275
<b>Crystallone</b>	F	Cut-glass imitation	Paul Schlochoff, Paris	CM-4
<b>Crystillin</b>	PF	t	Crystillin Products Corp., Brooklyn, N. Y.	CM-4
<b>Crystur</b>	UF	t	Panplastics, Heyden Chemical Co., Garfield, N. J.; American Plastics Corp., New York	PGB-3; CM-4
<b>Cumar</b>	Cumarone-indene	m, coatings, floor tile	Barrett Co., New York	APV-3, CM-4
<b>Cupren</b> (Cuprene)	Acetylene condensation product		Elektricitätswerke Lonsa, Basle, Switz.	CM-4; KPM275, K-2
<b>Cy-lent</b>		Gears	Timing Gear Corp., Chicago, Ill.	PGB-1
<b>Cygnat</b>	SR, F	m	Edison Swan Electric Co., Ltd., London, E. C. 4	CM-4
<b>D &amp; B</b>		Silent timing gears	Dalton & Balch, Inc., Chicago	PGB-1
<b>Dako</b>	?	m	Commercial Utilities, Ltd., London	CM-4
<b>Damarda</b>	PF	s, metal coating	Bakelite, Ltd., London, S.W. 1	BPY; CM-4
<b>Dartex</b>	Chlorinated rubber		Metallgesellschaft & Schiedeanstalt, Germany	CM-4
<b>Dayton Synthetic</b>	Petroleum hydrocarbon	Coatings	Dayton Synthetic Chemicals, Inc., Dayton, Ohio	APV-3
<b>Decora</b>	SR, casein	m	Universal Metal Products, Ltd., Lancas., England	BP, 1934, 6, 40
<b>Decoroid</b>			Howard Specialties Co., Inc., Brooklyn, N. Y.	PGB-1; CM-4

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Name	Composition	Forms, Uses	Company	Source
<b>Decosan</b>	?		Shanks & Co., Barrhead, England	CM-4
<b>Dekorit</b> (Decorite)	PF	t. amber substitute	Uhlhorn Bros., London, E.C. 1; Dr. F. Raachig G.m.b.H., Ludwigshafen, Germany; Herbert Doyle, Inc., Brooklyn, N. Y.	CM-4; BPY; PGB-1; BP; 1931, 2, 552
<b>Dentaglene</b>	F		Canadian Industries, Ltd., Montreal, Quebec	CM-4
<b>Dermatine</b> Same as <b>Fiber Diamond</b>				KPM276
<b>Detel</b>	Chlorinated rubber		International Patent Co., Detroit, Mich	CM-3
<b>Deverr</b>	SR		Ver Chem. Febr. Kreidl, Heller & Co., Vienna	BP, 1934, 6, 132
<b>Dexine</b>	Contains vulcanized rubber		Dexine, Ltd., London	Plastics, 1929, 5, 157
<b>Dexonite</b>	Acid- and alkali-proof rubber		Dexine, Ltd., London	Plastics, 1929, 5, 157; CM-4
<b>DI-EI</b>		Molding powder	H. Weidmann, Ltd., St. Gallen, Swits.	CM-4
<b>Diamond Fibre</b>	Vulcanized fiber	f	Continental-Diamond Fibre Co., Newark, Del	
<b>Diaphal</b>	UF			CGP, 1930, 27, 15217; CM-4
<b>Dilecto</b>	UF, PF	l, f	Continental-Diamond Fibre Co., Newark, Del	CM-4
<b>DilectoUF</b>	UF	l, f	Continental-Diamond Fibre Co., Newark, Del	CM-4
<b>Dinophene</b>	PF	s, m	Scott, Bader & Co., London, W C 2	APV-2
<b>Dioferrit</b>	PF & Maisine (dried & extracted corn)			KPM276; CM-4; K-3
<b>Dirigo</b>			Ohio Brass Co., Mansfield, Ohio	PGB-2; CM-4
<b>Dorex</b>	PF		Soc Dorex, Paris	CM-4
<b>Drybak Band Aid.</b> See <b>Revollite</b>	Cloth treated with PF		Johnson & Johnson, New Brunswick, N J	Plastics, 1933, 9, 21
<b>Dulux</b>	SR, modified alkyl	s	E. I. du Pont de Nemours & Co., Philadelphia; Nobel Chem. Finishes, Ltd., Slough, Bucks, England	CM-4
<b>Dumold</b>	Px	m	Du Pont Viscoloid Co., New York	CM-4
<b>Dundas</b>	Varnished fabrics		Mica & Insulating Supplies Co., Ltd., Melbourne, Victoria, Australia	BPY
<b>Duo-lite</b>	SG		Duplicate Corp., Pittsburgh, Pa.	CM-4
<b>Duprene</b> (DuPrene)	Oil-resisting rubber plastic from acetylene		E. I. du Pont de Nemours & Co., Wilmington, Del.	CM-4
<b>Duprenol</b>	Chlorinated rubber		Ver. Lackfabr.-Grau-Relino, Germany	CM-4
<b>Dura-C, 10 P and 10 R</b>	PF	s	Paramet Chemical Corp.; Stroock & Wittenberg Corp., New York	APV-3; CM-4; Chem. Markets, 1932, 36, 40
<b>Duradent</b>	UF	Denture	Bakelite Dental Supplies, London	CM-4; BP, 1932, 4, 186
<b>Duralac</b>		Lacquers	Sewall Paint & Varnish Co., Kansas City, Mo.	PGB-1

Name	Composition	Forms, Uses	Company	Source
<b>Duranoid</b>	PF with shellac		Specialty Mfg. Co., Hoosick Falls, N. Y.; Duranoid Co., Newark, N. J.	APV-2; CM-4
<b>Durat</b>	Same as Fibre Diamond			KPM276
<b>Durax</b>	PF	l	Isola-Werke, Düren, Germany	AR355; CM-4
<b>Durcoton</b>	Textile impregnated with PF		Meirowsky & Co., A.-G., Porz am Rhein, Germany	CM-4
<b>Durecol</b>	GP		Établissements Kuhlmann, Paris	CM-4
<b>Durez</b>	PF	m, s, f	General Plastics, Inc. North Tonawanda, N. Y.	APV-3; CM-4
<b>Durit</b>		Shellac substitute	Robt. Rauh, Inc., Newark, N. J.	PGB-1
<b>Durite</b>	PF	s, m	Durite Plastics Div., Stokes & Smith Co., Philadelphia	APV-2, 3; CM-4
<b>Durium</b>	Resorcinol-formaldehyde	m	Durium Products Corp., New York	APV-2, CM-4
<b>Duro-Kerit</b>	PF?		Plastika G m b H., Galalith Ges. Hoff, Harburg-Wilhelmsburg, Germany	CM-4
<b>Duroftal</b>	SR		Chem. Fab. Dr. Kurt Albert G m b H., Amoneburg-Weisbaden, Germany	CM-4
<b>Duroid</b>	PF		Soc. Française filiale de la Bakerite-Company, Plachy, France	CM-4; K-2
<b>Durolit</b>	PF	t	Soc. du Duroid, Enghien, France	CM-4
<b>Durolit</b>	?		Heko-Werke, Berlin-Tempelhof	CM-4
<b>Duropène (Duropene)</b>	Solid solution of trichlorisoprene in camphor		Peachy	KPM276; K-2; K-1
<b>Durophene</b>	PF	s, m	Scott, Bader & Co., London, W C 2	CM-4
<b>Duoprene</b>	Chlorinated rubber		A. H. Davis, Ltd., Liverpool	<i>Chem. Age (London)</i> , 1921, 4, 508
<b>Duoware</b>	UF, F	Ware	Beetle Products Co., Ltd., Worcestershire, England	K-2; CM-4
<b>Dux</b>	Alkyd resin		Nobel Chem. Finishes, Ltd., Slough, England; E. I. du Pont de Nemours & Co., Wilmington, Del.	CM-4; APV-2
<b>Ebénit</b>	X, substitute for "Bois-durci" (blood albumin compound)		Établissements Grivolais, Paris	CM-4; KPM276; K-2
<b>Ebonestos</b>	?	m, articles	Ebonestos Insulators, Ltd., London, S.E. 15	BPY; CM-4
<b>Eborin</b>	Gum compound		Soc. Beguin, Paris	PGB-1
<b>Eburin</b>	X	Hot molding	Soc. Beguin, Paris; I. G. Farbenind. A.-G., Frankfurt, Germany	K-2; CM-4; H179
<b>Écaille 97%</b>	PF	t	Labs. Ind. d'Asnières, Paris	CM-4
<b>Edekreanol</b>	SR		Resan Kunststoffsabrik A.-G., Vienna	CM-4
<b>Elastica</b>	SG, SR interlayer		I. G. Farbenind. A.-G., Frankfurt, Germany	CM-4
<b>Elastolith</b>	PF	t	Herold A.-G., Hamburg, Germany	BPY; CM-4; AR337



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Name	Composition	Forms, Uses	Company	Source
<b>Elbolit</b>	SR		L. Brüggemann, Hellbron, Germany	CM-4
<b>Elbenit</b>	SR		L. Brüggemann, Hellbron, Germany	CM-4
<b>Elbolit</b>	SR		L. Brüggemann, Hellbron, Germany	CM-4
<b>Electrobestos</b>	X	Cold molding	Johns-Mansville, Inc., New York	PGB-1; CM-4; H179
<b>Electroine</b>			Établissements Grivolos, Paris	PGB-2; CM-4
<b>Electrolite</b>	Gum compound		Établissements Grivolos, Paris, France	PGB-1
<b>Electrose</b>	X	Hot molding	Insulator Mfg. Co., Brooklyn, N. Y.	CM-4
<b>Elephantide</b>		Laminated board	Mica & Insulating Supplies Co., England	CM-4
<b>Elfbelmaché</b>	?SR	l, papier maché		KPM277; CM-4
<b>Elfenite</b>	Resin adhesive		C. Werfel	APV-2; CM-4
<b>Ellinol</b>	?SR	m	Ellison Insulations, Ltd., Birmingham, England	KPM277; CM-4
<b>Ellison Laminated</b>	PF	l, gears	Ellison Insulations, Ltd., Birmingham, England	BPY
<b>Elimar</b>	?SR	m	Elimar Mouldings Co., Birmingham, England	KPM277; CM-4
<b>Elo</b>	PF	s, m, l	Birkbys, Ltd., Liversedge, Yorks., England	CM-4; APV-2
<b>Empire</b>		Insulating materials	Mica Insulator Co., New York	PGB-1
<b>Endura</b>	JF, F	Ware	Beetle Products Co., Ltd., Worcestershire, England	Plastics, 1927, 3, 806; K-2; CM-4
<b>Eolit, formerly Juvellith</b>	PF	t	Établissement Kuhlmann, Paris; Kunsttharsfabrik Dr. F. Pollak, Vienna	KPM277; CM-4
<b>Epok</b>	SR	s, m	British Resin Products, Ltd., Kingston, Surrey, England	BPY; CM-4
<b>Ergolith</b>	C		McLeod & McLeod, London, W.C. 1	BPY; CM-4
<b>Ericon</b>	PF	l, panelling	Merritt Eng. & Sales Co., Lockport, N. Y.	CM-4
<b>Erinite</b>	SR	s	Erinoid, Ltd., London, E.C. 2	CM-4
<b>Erinofort</b>	CA	f, m	Erinoid, Ltd., London, E.C. 2	CM-4
<b>Erinoid</b>	C	f	Erinoid, Ltd., London, E.C. 2; Mica & Insulating Supplies Co., Melbourne, Victoria, Australia; American Plastics Corp., New York	CM-4; BPY
<b>Erinol, O &amp; P</b>	PF, resin intermediate		Erinoid, Ltd., London, E.C. 2	APV-2; CM-4
<b>Erinopol</b>		Dip polish for casein & horn materials	Erinoid, Ltd., London, E.C. 2	BPY
<b>Ernolith</b>	Yeast-aldehyde		Blücher & Krause, Leipsig, Germany	CM-3; KPM277
<b>Eshalite (Eshalite)</b>	? sebestos, zinc carbonate and powdered coal	m	Marsahn & Fritsch Siemens-Schuckert Werke A.-G., Berlin	KPM277; CM-4
<b>Esterol</b>	Alkyd and modified alkyd resin	Coatings	Paramet Chemical Corp; Stroock & Wittenberg Corp., New York	APV-2, 3; CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Esterpol</b>	SR		Glyco Products Co., Inc., Brooklyn, N. Y.	CM-4
<b>Extrakitt</b> (Estralite)	PF			<i>Plastics</i> , 1930, <b>6</b> , 705; CM-4; AR347
<b>Fawellit</b>	Asbestos and binder		Siemens-Schuckert-Werke G.m.b.H.	KPM277; CM-4
<b>Ethanite</b>	Ethylene-dichloride and Ca polysulphides	Oil-proof rubber substitute	Wilfred Smith, Ltd., London, W.C. 3.	CM-4; BP, 1933 <b>4</b> , 391, 440
<b>Euboolith</b>	IB	Flooring material	Soc anon. Euboolith, Paris	CM-4
<b>Evaplastin</b>	F		Evered & Co., Ltd., England	CM-4
<b>Extraplast</b>		Insulators	Vorwerk & Sohn, Wuppertal-Barmen, Germany	CM-4
<b>Fabrigear</b>		Silent gears	Dalton & Balch, Inc., Chicago	PGB-1
<b>Fabroll</b>	PF	Gears	General Electric Co., Schenectady, N. Y.; British Thomson-Houston Co., Rugby, England	CM-4
<b>Fabrolite</b>	PF	m	British Thomson-Houston Co., Ltd., Rugby, England, Commercial Utilities, Ltd., London	BPY, CM-4
<b>Fantasit</b> (Fantasite)	UF		Rhen-Westfal Sprengstoff A.-G., Troisdorf, Germany	CM-2; AR408
<b>Faollite</b>	PF and asbestos			<i>Chem. Abs.</i> , 1935, <b>29</b> , 3060
<b>Farlite</b>	PF	l	Farley & Loetscher Mfg. Co., Dubuque, Iowa	CM-4
<b>Faturan</b>	PF	f	Dr. Heinrich Traun & Söhne and Herold Akt. Ges., Hamburg, Germany	BPY; CM-4
<b>Fermit</b>	?	m		GZ, 1931, <b>45</b> , 1010, CM-4
<b>Ferrosell</b>	PF?	l	Deutsche Ferrosell G.m.b.H., Augsburg, Germany	K-2, CM-4
<b>Festollan</b>	F, SR, Px		Allgem. Elektrizitäts-Ges., Berlin	K-5
<b>Fiber Diamond</b>	Gutta-percha subst. with powdered sulphur, antimony sulphide, iron oxide, asbestos, zinc oxide and sulphate, clay and ammonium carbonate		Dermatine Ltd., London	CM-4, KPM278
<b>Fiberlac</b>	Px	Lacquers, enamels	Fiberloid Corp., Indian Orchard, Mass.	BPY
<b>Fiberloid</b>	Cellulose nitrate and acetate		Fiberloid Corp., Indian Orchard, Mass.	CM-4
<b>Fiberlon</b>	PF	t	Fiberloid Corp., Indian Orchard, Mass.	CM-4
<b>Fibestos</b>	CA, SG	f	Fiberloid Corp., Indian Orchard, Mass.	BPY; CM-4
<b>Fibrocc</b>	PF	f, l	McLeod & McLeod, London, W.C. 1.; Fibrocc Insulation Co., Valparaiso, Ind.	PGB-1; BPY
<b>Fibros</b>	PF	l, s	U. S. A.	NSR122
<b>Fimielite</b>	PF		Italy	<i>Plastics</i> , 1929, <b>6</b> , 587; CM-4
<b>Firmoid</b>	CA, Px		Bluemel Bros., Ltd., Wolston, England	BPY; CM-4; KPM278

# TRADE NAMES LIST

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Name	Composition	Forms, Uses	Company	Source
<b>Flexbestos</b>	SR, asbestos	Brake linings	H. Trist & Co., Bristol, England	BP, 1934, 6, 224
<b>Flexo</b>	Resins		Glyco Products Co., Inc., Brooklyn, N. Y.	CM-4
<b>Flexoresin GG-1 and E-1</b>	Polymerized terpene resins	Modifiers	Glyco Products Co., Inc., Brooklyn, N. Y.	Plastics
<b>Formalite</b>	PF		Bakelite, Ltd., Greet, England	CM-4
<b>Formapex Miocarta</b>			Ioco Rubber & Waterproofing Co., Ltd., Glasgow, Scotland; Mica & Insulating Supplies Co., England	CM-2
<b>Formica</b>	PF, UF	l	Formica Insulation Co., Cincinnati, Ohio	CM-4
<b>Formita</b>	PF		Bakelite Corp., New York	K-2
<b>Formite</b>	PF	t	Bakelite, Ltd., London, S W. 1.	BPY; CM-4
<b>Formolit</b>	?	m	Hamburger Gummi-Waren Compagnie, Hamburg, Germany	CM-1
<b>Formolit (Formolite)</b>	X		Alexander M. Nastukoff, Moscow	K-2; CM-1
<b>Formvar</b>	Polyvinyl acetate-methylal	Coatings, adhesives	Shawinigan Chemicals, Ltd., Montreal, Quebec; Shawinigan Products Corp., New York	CM-4; J.S.C.I., 1934, 52, 614; BP, 1934, 6, 132
<b>Futan Futon</b>	?	Articles	Cable Mfg. Co., Ltd., Bratislava, Czechoslovakia	BPY
<b>Futurit</b>	PF		Kabelfabrik & Draht Ind., Wien; Kabelgyar-Werken, Hungary	CM-4
<b>Fybroid</b>	Insulating paper		Wilmington Fibre Specialty Co., Wilmington, Del.	PGB-1
<b>G and E</b>		Insulation	Görner & Engels, Dresden	CM-4
<b>G. E. E.</b>	Ebonite sheets		McLeod & McLeod, London, W.C. 1	K-6
<b>Galakellite</b>				PGB-2
<b>Galalith (Galalithe)</b>	C		Galalith, Ltd., London; Internationale Gal. Ges. and Hoff & Co., Harburg, Germany	KPM278; CM-4
<b>Galatix</b>		m	Lumos & Co., London	Plastics, 1929, 5, 157
<b>Galley's Dental Resin</b>			John U. Galley & Co., New York	PGB-2
<b>Gallia-Rubber</b>	Rubber base plastic		Manufacture d'Isolants & Objets Moulés, Vitry, France	BPY; CM-4
<b>Gansolite</b>	?		Gansolite, Ltd., Nijkerk, Netherlands	CM-4
<b>Gardlite See Santolite</b>	Toluene sulphonamide-formaldehyde		Monsanto Chemical Co., St. Louis, Mo.	APV-3
<b>Geaphtal</b>	GP		Allgem. Elektrizitäts-Ges., Berlin	APV-2; CM-4; K-5
<b>Geax</b>	PF	l		AR355
<b>Gédélite</b>	Phenol-, cresol-formaldehyde		Soc. Huiles, Goudrons et Dérivées, Paris	CM-4
<b>Geloid</b>	Gelatin base		Urbain Thuau, Germany	PGB-2; CM-4
<b>Gelva</b>	Polyvinyl acetate	Coatings, plastics, adhesives	Shawinigan Chemicals, Ltd., Montreal, Quebec; Shawinigan Products Corp., New York	CM-4
<b>Gemstone</b>	PF	t	A. Knoedler Co., Lancaster, Pa.	CM-4
<b>Genclvex</b>	PF	Denture		CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Geolith</b> (Geolithe)	78R			KPM278; K-3
<b>Glider</b>	F, CA?	m	A. W. Kanis, London; Crayonne, Ltd., Bexley, Kent, England	BPY; CM-4
<b>Glorit</b>	C		Schiel & Spol Sternberg, Czechoslovakia	PGB-2; CM-4
<b>Glutol</b>	SR		U. S. S. R.	CM-4
<b>Glutoline SI100</b>	Methyl cellulose ether		Advance Solv. & Chem. Corp., New York	
<b>Glycolac</b>	GP		Établissements Kuhlmann, Paris	CM-4
<b>Glycolite</b>	PF, UF	m	Glycolite Co., New York; Glyco Research Labs., Phila., Pa.	PGB-3; CM-4
<b>Glycopon</b>	Condensation product of glycols		Glyco Products Co., Inc., Brooklyn, N. Y.	K-3
<b>Glyptal</b> (Glyptale)	GP		General Electric Co., Schenectady, N. Y.; Bakelite G.m.b.H., Berlin	CM-4; APV-2; KPM278; K-3
<b>Glyptanite</b>	Glyptal-bonded mica		Micanite & Insulators Co., Ltd., London, E. 17	APV-2; BPY
<b>Gramaphoid</b> (Gramaphaoid)	?	Records	General Plastics Corp., Ltd., London, S.E. 13	CM-4; <i>Plastics</i> , 1933, 8, 466
<b>Greif Faturan</b>	PF	f	Herold A.-G., Hamburg, Germany	KPM279
<b>Gual-A-phenic</b>	Turpentine by-product		Wood Chemical Products Co., New York	PGB-3
<b>Gummite</b> (Gummithe)	Bituminous	Insulation	Manufacture d'Isolants & Objets Moulés, Vitry, France; Cie. Générale d'Electricité, France	CM-4; BPY; PGB-2; KPM 279
<b>Gummoid</b>	Paper and textile base	Articles	Cable Mfg. Co., Ltd., Bratislava, Czechoslovakia	BPY
<b>Gummon</b>	F, PF, bitumen, rubber	cold molding	Garfield Mfg. Co., Garfield, N. J.; Rhein. Westf. Sprengstoff A.-G., Troisdorf; Isolatoren-Werke, München, Germany	K-3; CM-4; KPM279
<b>H. V.</b>		Laminated plastic sheets	McLeod & McLeod, London, W.C. 1	BPY
<b>Haefelyte</b>	C, PF	t	Emil Haefely & Cie., Basle, Switz.	CM-4
<b>Halex</b>	?	Ware	British Xylonite Co., London	CM-4
<b>Halisite</b>	PF		Halisite Corp., New York	CM-4
<b>Halolume</b>	CA		British Electrical Installations Co., London	APV-2; CM-4
<b>Halowax</b>	Chlorinated naphthalenes		Halowax Corp., New York	CM-4
<b>Hares</b> (Haresite Haresplatten Harox, Harex)	PF	s, m, l	H. Römmler A.-G., Spremberg, Germany	APV-2; CM-4; K-4
<b>Harest Platten</b>	PF	l	H. Römmler, A.-G., Spremberg, Germany	CM-4
<b>Harex</b>	PF	l	H. Römmler, A.-G., Spremberg, Germany	CM-4
<b>Harlequin</b>	UF, F		Beetleware Corp., New York	CM-4; K-3
<b>Harvel</b>	Cashew nut derivative		Harvel Corp., Irvington, N. J.	
<b>Harvite</b>	UF	m	Watertown Mfg. Co., Watertown, Conn.	PGB-3
<b>Haakelite</b>	PF	l, panelling	Haakelite Mfg. Corp., Chicago	CM-4

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Name	Composition	Forms, Uses	Company	Source
<b>Haveg</b>	PF-asbestos	Building material	Haveg Corp., Newark, Del.; Säureschutz G. m. b. H., Berlin	CM-4; K-4; Plastics, 1933, 9, 19
<b>Hecolite</b>	Px	Dentures	American Hecolite Denture Corp.	Plastics, 1933, 9, 158
<b>Hekolith</b> (Hecolithe)	Plastic composition		Heko-Werk Chemische Fabrik A.-G., Grünwald, Germany	PGB-1; CM-4
<b>Hellosit</b>	PF?	Insulating resins	Kontakt-Römmeler A.-G., Frankfurt, Germany	K-3; CM-4
<b>Hemcoware</b>	UF, F		Bryant Electric Co., Bridgeport, Conn.	CM-4
<b>Hemit</b>		Insulation	Garfield Mfg. Co., Garfield, N. J.	PGB-1
<b>Heptene Base</b>	Aniline-Heptaldehyde		Naugatuck Chem. Co., Naugatuck, Conn.	CM-4
<b>Herculite</b>	PF, X	m	Colasta Co., Hoosick Falls, N. Y.	PGB-3, CM-4
<b>Herkolite</b>	PF?	Insulation	General Electric Co., Schenectady, N. Y.	PGB-3; CM-4
<b>Herolith</b>	PF General Trade-Mark covering Elastolith, Marbolith, Faturan, g.s.	t, s	Herold A.-G., Hamburg, Germany	CM-4; BPY; Syn. Appl. Fin., 1931, 2, 89
<b>Heureka</b>	PF	Denture		CM-4
<b>Hévénold</b>	Rubber, sulphur and camphor		Gerner	KPM279; CM-4; K-3
<b>Hightensite</b>	?		Hightensite, Ltd.	BP, 1930, 2, 280; CM-4
<b>Homac</b>	SR		Walton Chem. Co., Ltd., Liverpool, England	CM-4
<b>Hopan</b>			Kunstharzfabrik Dr. F. Pollak, Vienna	PGB-1
<b>Hycoloid</b>	Px, CA		Hygienic Tube & Container Co., Newark, N. J.	Plastics, 1931, 7, 262; CM-4
<b>Hydroresin</b>	SR	Sticky, non-drying	Glyco Products Co., Inc., Brooklyn, N. Y.	
<b>Hyll</b>	Px, F		Hygienische Ind. G., Ostortag, Ludwigsburg, Germany	CM-4
<b>I. C. I. Moulding Powders</b>	PF	m	Imperial Chem. Industries, Ltd., London, S.W. 1	CM-1
<b>Iherolithe</b>	PF		Soc. l'Orolithe, Rueil, France	CM-2
<b>Idelite</b>	PF		Bakelite, Ltd., London, S.W. 1	BPY; CM-4
<b>Iditol</b>		Shellac substitute	U. S. S.R.	CM-4
<b>Idonite</b>	PF	t	Damard Lacquer Co., Ltd., Birmingham, England	
<b>Idytol</b>	PF			RGP, 1932, 8, 295; CM-4
<b>Imperial E. K. Gum</b> <b>Imperial Fat Gum</b>		Coatings	J. D. Lewis & Co., Providence, R. I.	APV-3
<b>Imperial Ester</b>		Coatings, linoleum	J. D. Lewis & Co., Providence, R. I.	APV-3
<b>Impermo</b>	PF, F	Containers	F. L. Stoffel, Arbon, Swits.	BP, 1934, 6, 317
<b>Inerinit</b>		Insulation	Christiani & Nielsen, Hamburg, Germany	CM-4
<b>Inda</b>			Amer. Machine & Foundry, Co. Brooklyn, N. Y.	PGB-2; CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Indur</b>	Phenolic SR		International Tar & Combustion Co.; Reilly Tar & Chemical Co., Indianapolis, Ind.	PGB-3
<b>Indurite</b>	PF	m	"Indurite" Sales, Ltd., London	CM-4
<b>Industrol</b>	SR		Établissements Kuhlmann, Paris	CM-4
<b>Infuselax</b>	UF	Wood-lacquer	Beetle Products Co., Ltd., London	APV-2; CM-4
<b>Infusite</b>	Heat-resisting molding material. Mineral binder		Manufacture d'Isolants et Objets Moulés, Vitry, France	CM-4; BPY
<b>Inlite</b>	X, asphaltic base	f	Inland Mfg. Co., Dayton, Ohio	CM-4
<b>Inodite</b> See <b>Ondolite</b>				CM-4
<b>Insulate</b>	X	Hot molding	Insulation Mfg. Co., Brooklyn, N. Y.	CM-4
<b>Insultit</b>	W		Backus-Brooks Co., Minneapolis, Minn.	CM-4; K-2
<b>Insulite</b>			Insulation Mfg. Co., Brooklyn, N. Y.	PGB-2
<b>Insuloid</b>	CA	Bands	American Products Mfg. Co., New Orleans, La.	K-3; CM-4
<b>Insurok</b>	PF	l	Richardson Co., Melrose Park, Ill.	PGB-3, CM-4
<b>Invellith</b>	PF		Kunstharsfabrik Dr. F. Pollak, Vienna	NSR118, 179
<b>Irgonite</b>	SR		J. R. Geigy S. A., Basle, Switz.	CM-4
<b>Isogallithe</b> (Isogallithe)	C		Garraud, Taillebourg, France	PGB-2; KPM279; K-1
<b>Isolémail</b>	SR	s	Soc. des Laques & Isolants, Lyons, France	CM-4
<b>Isolid</b>	PF		Soc. Française, Lyons, France	K-1; CM-1
<b>Isolierstahl</b>	PF			Plastics, 1930, 6, 705; CM-4
<b>Isolite</b> (Isohit)	PF	s, l	Soc. Française, Lyons, France	PGB-1; K-1; K-3
<b>Isolithe</b> (I-olithe)	PF?		Soc. Française, Lyons, France; Soc. Beguin, Paris	CM-4; K-1; K-3
<b>Isoloid</b>	CA		Charles Martin, Lavallois, France	APV-2; CM-4
<b>Isophan</b>	Ethyl cellulose	P	Cellonwerke, Charlottenburg, Germany	CM-4
<b>Isoplac</b>		Insulation	Soc. Isoplac, Paris, XVII	CM-4
<b>Isotex</b>	SR		Soc. l'Asbestite, Paris	CM-4
<b>Issolin</b>	SR	s		CM-4
<b>Issolin</b>	PF	Shellac substitute	Dresden	NSR124, 118; AR283
<b>Issolith</b>	SR			KPM279; CM-4
<b>Issolith Resol</b>	PF	s		KPM280; AR324; K-3
<b>Itoco</b>	PF	Denture		CM-4
<b>Ivaleur</b>	PF	t	Celluloid Corp., Newark, N. J.	CM-4
<b>Ivolt</b>	UF	m	Soc. Beguin, Paris	PGB-2
<b>Ivolt</b>	PF	t	Établissements Kuhlmann, Paris	CM-4
<b>Ivolt</b>	PF	t	Kunstharsfabrik Dr. F. Pollak, Vienna	CM-1

Name	Composition	Forms, Uses	Company	Source
<b>Ivolt-Opal</b>	PF	t	Établissements Kuhlmann, Paris	CM-4
<b>Ivorax</b>	PF	t	Herold, A.-G., Hamburg, Germany	CM-4
<b>Ivorlold</b>	PF	f, t		<i>Modern Plastics</i> , 1935, 12(9), 54
<b>Ivrit</b>	PF	t	Établissements Kuhlmann, Paris	CM-2
<b>Ivrite</b>	PF		Soc. Anon. Ivra, Torino, Italy	CM-4
<b>Ixolain</b>	Phenolic base	Denture	Ixolain Ges., Germany	CM-4; <i>Plastics</i> 1927, 3, 551
<b>JMS</b>	?SR		Chemie & Technik J.M.S. G.m.b.H., Hamburg, Germany	K-3, CM-4
<b>Jacelite</b>		f	J. A. Crabtree & Co., Ltd., Walsall, England	CM-4
<b>Jarax</b>	PF	l	Jaroslawa's Glimmer-Waren- Fabrik, Berlin	CM-4
<b>Jaxolite</b>	PF, F		Cie Ind. de Mécanique Horlogerie, Paris	CM-4
<b>Jevanolite</b>	GP, wood rosin		*	APV-1
<b>Jevelite</b>	PF, with talc powder		Kunstharsfabrik Dr. F. Pollak, Vienna	KPM280
<b>Jewelin</b>	PF	t	Jewelin Corp., Woodside, N. Y.	CM-4
<b>Joanite</b>	PF	t	Joanite Corp., Long Island City, N. Y.	K-3; CM-4
<b>Jonite</b>	W		Akt. Torefors Sagverk, Sweden	CM-4
<b>Jurid</b>	?asbestos filler	m	Kirchbach, Germany	CM-4
<b>Juvelith</b> (Juvelit)	PF	t	Kunstharsfabrik Dr. F. Pollak, Vienna, Établissement Kuhl- mann, Paris	KPM280; CM-4
<b>K-M</b> See <b>Resin KM</b>	SR	s	Advance Solvents & Chemical Corp., New York	CGP, 1933, 30, 16591; CM-4
<b>Kabelit</b>	SR		Bredovska, Czechoslovakia	PGB-2, CM-4
<b>Kalanite</b>	Bituminous	Insulator	Callender's Cable & Const. Co., Ltd., London	K-6, CM-4
<b>Karben</b> See <b>Kupren</b>	Acetylene con- densation prod- uct		Elektrizitätswerke Lanza, Basle, Switz.	K-3; CM-4
<b>Karbolite</b>	PF with naph- thalene sul- phonic acids		U. S. S. R.	<i>Plastics</i> , 1926, 2, 391, 436; CM-1; PGB-2; K-3
<b>Karolith</b>	C	f, m	American Plastics Corp., New York; Karolith Corp., Long Is- land City, N. Y.	CM-4
<b>Kaurit</b>	UF in aqueous sol.	Binder	I. G. Farbenind. A.-G., Frankfurt, Germany	
<b>Kaynite</b>		m	Waterbury Button & Mfg. Co., Waterbury, Conn.	PGB-1
<b>Keebush</b>	PF resin and acid-resistant compound		Kestner Evaporator & Engi- neering Co., London, S.W.	CM-4
<b>Kelacoma</b>	UF, F, PF	m, tiles and cement	Kelacoma Ltd., Welwyn, Gar- den City, England	KPM280; BPY, CM-4
<b>Kellite</b>	PF		Kellogg Switchboard & Supply Co., Chicago	CM-4
<b>Kerit</b>	C, F		Internationale Galalith Ges., Harburg-Wilhelmsburg, Ger- many; Galalith, Ltd., London	CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Kilhanit</b>	PF or GP		Bakelite G.m.b.H., Berlin	K-5; CM-4
<b>Kodaloid</b>			Eastman Kodak Co., Rochester, N. Y.	PGB-2
<b>Kodapak</b>	CA	Sheet, P	Eastman Kodak Co., Rochester, N. Y.; Tennessee Eastman Co., Kingsport, Tenn.	CM-4
<b>Koken</b>	SR		Nippon Paint Co., Ltd., Japan	CM-4
<b>Kollnit</b>	Lignite, cresol		Studien & Verwertungs G.m.b.H., Mülheim, Germany	CM-4; BP, 1933, 4, 445
<b>Komac</b>	Coal-tar pitches		American Tar Products Co., Pittsburgh, Pa.	
<b>Kopan</b>	PF	m, s	Kunstharzfabrik Dr. F. Pollak, Vienna	APV-2; CM-4
<b>Kopol</b>	SR		Beck, Koller & Co., Inc., Detroit, Mich.	CM-4
<b>Koraton</b>	PF	t	Wedig & Reuss, Eilenburg, Germany	CM-4
<b>Koroseal</b>	Modified vinyl halide polymer	m, f	B. F. Goodrich Co., Akron, Ohio	<i>Ind. Eng. Chem.</i> , 1935, 27, 667; BP, 1935, 7, 55.
<b>Kupren</b>	Acetylene condensation product		Elektrizitätswerke Lonsa, Basle, Switz.	CM-4; K-3
<b>Kurlac</b>		Shellac substitute	E. I. du Pont de Nemours & Co., Wilmington, Del.	PGB-1
<b>Kylold</b>	C		Kylold Co., Muskegon, Mich.	PGB-2; CM-4
<b>Lacalite</b> (Lacalith, Lacaulite, Lacaulith)	SR		Soc. d'Appl. des Goudrons & Dérivés, Paris	CM-4
<b>Lacante</b>	PF, shellac base		American Record Corp., Scranton, Pa.; Scranton Button Co., New York	CM-4; PGB-3
<b>Laccain</b>	PF		Louis Blumer, Zwickau, Germany	CM-4
<b>Lacrinite</b>	C, PF	f	Lacrinoid Products, Ltd., London, E. 7	CM-4; BPY
<b>Lacrinoid</b>	F	Artificial horn	Lacrinoid Products, Ltd., London, E. 7	CM-4
<b>Lactit</b>	C, boric acid and lead acetate			K-3
<b>Lactite</b>	C (hydrated casein, alum, borax, starch)			CM-4; K-3
<b>Lactitis</b>	C, metallic caseinate			CM-4
<b>Lactoid</b>	C	f	British Xylonite Co., England	CM-4
<b>Laculose H, A, B</b>	GP	s	Grindley & Co., Ltd., London, E. 14	APV-2; CM-4
<b>Lakilac</b>	PF	m	Jos. Lucas, Ltd., Birmingham, England	CM-4
<b>Lamicaid</b>	PF, UF	l	Mica Insulator Co., Chicago	PGB-3; CM-4
<b>Laminel (Lenninol)</b>	PF	l	Ellison Insulations, Ltd., Birmingham, England	KPM281; CM-4
<b>Laminar</b>	Vulcanised fiber product		National Vulcanised Fibre Co., Wilmington, Del.	PGB-1
<b>Laminite</b>			Old King Cole, Inc., Canton, Ohio	PGB-1
<b>Lamson's Gum</b>	Pitch from hardwood distillation	Shellac composition	Lamson Trading Co., Newark, N. J.	



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Name	Composition	Forms, Uses	Company	Source
<b>Lastilac</b>		m	Jos. Lucas, Ltd., Birmingham, England	CM-4
<b>Lennite</b>	PF	Dentures	Ohio Chemical & Mfg. Co., Cleveland, Ohio	CM-4; <i>Plastics</i> , 1927, 3, 552
<b>Leolan</b>	D		Leo-Werke, G.m.b.H., Dresden, Germany	CM-4
<b>Leuchtol</b>	SR		Nippon Resin Kogyo Co., Ltd., Japan	CM-4
<b>Leukon</b>	SR	m, f	Imperial Chemical Industries, London, S.W. 1	BP, 1935, 6, 440
<b>Leukorit</b>	PF	t	Uhlhorn Bros., London E.C. 1; Dr. F. Raschig, G.m.b.H., Ludwigshafen, Germany	BP, 1931, 2, 552; CM-4; BPY
<b>Lewisol</b>	Modified alkyd resins	Coatings	J. D. Lewis & Co., Providence, R. I.	APV-3; CM-4
<b>Lignat</b>	W		Cristof & Unmack A.-G. Oberlausitz, Germany	CM-4; K-3
<b>Linapex</b>		Varnished fabrics	Mica & Insulating Supplies Co., Ltd., Melbourne, Victoria, Australia	BPY
<b>Linax</b>	PF	l		CM-4
<b>Lindaleur</b>		f	Celluloid Corp., Newark, N. J.	PGB-1
<b>Linga-Longa</b>	UF	f, ware	Beatl Sales Co., London; C. Hughes, Birmingham, England	CM-4; BPY
<b>Linolin</b>	?	Insulation	Lindsey & Williams Ltd., Manchester, England	CM-4
<b>Lionite</b>			Lionite Insulation Corp., Brooklyn, N.Y.	PGB-1
<b>Litholite</b>	?	Molded articles	Litholite Insulators Ltd., London, E. 8	BPY
<b>Lochron</b>	UF in alk. soln.	Applied with an acid salt for fire-proofing	I. G. Farbenind A.-G., Frankfurt, Germany	
<b>Locron</b>	UF	s	I. G. Farbenind A.-G., Frankfurt, Germany	CM-4
<b>Lonarit</b>	CA	m	Lonarit G.m.b.H., Berlin; Rheinisch-Westfälische Sprengstoff-Fabrik, Germany	BP, 1932, 3, 521; CM-4; KPM281
<b>Lor-Wal-Lith</b>	PF	t	Chemie & Technik J. M. S. G.m.b.H., Hamburg, Germany	CM-4; K-3
<b>Lorival</b>	PF	t, m	Lorival Mfg. Co. Ltd., Southall, England	BPY; CM-4 K-6
<b>Low Bake</b>	SR	Coatings	Nobel Chemical Finishes Ltd., Slough, England	K-6
<b>Lucienit</b>	PF	t	Lucien Eilertsen	KPM282; CM-4
<b>Lucite</b>	Px	f	Du Pont Viscoloid Co., Arlington, N. J.	CM-4
<b>Ludomite (Lugdomite)</b>	CA		Soc. Lyonnaise de Celluloids, Lyons, France	APV-2; CM-4
<b>Luglas</b>		SG with a resin center sheet	Sicherheitsglas G.m.b.H., Kunsendorf, Germany	CM-4
<b>Lumarith</b>	CA	m	Celluloid Corp., Newark, N. J.	CM-4
<b>Lupinit</b>	C		Lupinit, G.m.b.H., Mannheim, Germany	CM-4
<b>Lusterloid</b>	Px	P, f	Silcock-Miller Co., South Orange, N. J.	PGB-3; CM-4
<b>Lustilac</b>		m	Jos. Lucas, Ltd., Birmingham, England	CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Luxan</b>	UF	s	Luxite, Inc., Boston, Mass.	APV-2; CM-4
<b>Luxene</b>	PF	Denture	Ransom & Randolph, Toledo, Ohio; Bakelite Corp., New York	CM-4
<b>Luxite</b>	UF, PF, F	s, m	Luxite, Inc., Boston, Mass.	CM-4
<b>Luxolith</b>	C		Soc. l'Oyannaxienne, Oyannax, France	PGB-2; K-1
<b>ML Beatiware</b>	UF, F	Ware	Billmyre Mfg. Co., Ltd., London; Beati Sales Ltd., London	CM-4
<b>Macold</b>	Px	Dip finish	Crawford, MacGregor & Canby, Dayton, Ohio	PGB-3; CM-4
<b>Magranit</b> (Magranite)	PF	l, s	Australia	APV-2; CM-4, PGB-2
<b>Malsine</b>	Dried and extracted corn	Celluloid substitute		KPM282; CM-4
<b>Maizewood</b>	W, cornstalk board		Maizewood Products Corp., Dubuque, Iowa	Ce, 1930, 1, (9) (10); CM-4
<b>Maizolith</b>	Resinous material from cornstalks by treatment with caustic soda		Prepared by U. S. Bureau of Soils and Iowa State College	RGP, 1930, 6, 461; BP, 1930, 2, 31; CM-4, KPM282
<b>Makalot</b>	PF	s, m	Makalot Corp., Boston, Mass.	APV-2, CM-4
<b>Maklodone</b>	Hard rubber plastic		McLeod & McLeod, London, W. C. 1	KPM283
<b>Malcase</b>	PF			RGP, 1932, 8, 157; CM-4
<b>Mandem</b>	Ebonite	f	McLeod & McLeod, London, W. C. 1	K-3; CM-4
<b>Marbalin</b>	PF, ?	f	Federal Cutlery Co., New York	CM-4
<b>Marblette</b>	PF	t	Marblette Corp., Long Island City, N. Y.	CM-4
<b>Marbloid</b>	CA		Speights, Ltd., England	K-3
<b>Marbloid</b>	UF		Dai-Nippon Celluloid Co., Ltd., Sakai, Japan	BPY
<b>Marbolith</b>	PF	t, f	Herold A.-G., Hamburg, Germany	CM-4, BPY
<b>Margolit</b>		Cold molded	Ver Isolatorenwerke A.-G., Germany	CM-4
<b>Margressit</b>	F, PF, UF, with asbestos-cement sheets		Philips Industrial, London, W. C. 2	BPY
<b>Marvelex</b>		SG	England	PGB-2, CM-4
<b>Masa</b>	PF	l	Masa, G.m.b.H., Berlin	K-3, CM-4
<b>Masonite</b>	W		Masonite Corp., Laurel, Miss.	CM-4
<b>Mastol</b>	PF	s	Symmentis Products, Ltd., Eccles, England	CM-4
<b>Mastolite</b>	PF	l	Symmentis Products, Ltd., Eccles, England	CM-4
<b>Masuron</b>	CA	f, m	John W. Masury and Sons, Brooklyn, N. Y.	CM-4
<b>Mayfair</b>	78R	Molded hardware	Harrison Bros., Birmingham, England	BPY
<b>Megohmax</b> (Megohmior)	PF, mica	Insulation	John Moores & Co., Salford, Lancas., England	AR355; CM-4 Plastics, 1930, 6, 705

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Name	Composition	Forms, Uses	Company	Source
<b>Megohmit</b> C. O. M.	Mica-linen and paper	Insulation	Meirowsky & Co. A.-G., Pors, Germany	BPY
<b>Megohmo</b>		Molded insulation	Waterbury Button & Mfg. Co., Waterbury, Conn.	PGB-1
<b>Meigsoid</b>	Sugar-aniline		Meigsoid Corp., Jersey City, N. J.	CM-4
	Silica-clay, powdered filler	m	F. W. Buk & Co., New York	
<b>Meluzite</b>	PF		France	NSR118
<b>Membranit</b>	Aqueous alkyd emulsion			CM-4; APV-2
<b>Metakalin</b> (Metakaline)	PF	Shellac substitute		RGP, 1932, 8, 157; AR283; CM-4; NSR118, 124
<b>Metduro</b>	PF	t	Metduro, Ltd., London	Plastics, 1929, 5, 294; CM-4
<b>Metropole</b> See Metduro				
<b>Micabond</b>	GP, mica	f, articles, l	Continental-Diamond Fibre Co., Newark, Del.	
<b>Micafolium</b>	PF, mica	l		Plastics, 1930, 6, 705; CM-4; AR355
<b>Micalas</b>	Mica	l	Soc. Francaise le Micalas, France; J. Moores & Co., Salford, England	CM-4
<b>Micanite</b> (a) Hard (b) Molding (c) Flexible	Shellac-bonded mica 3-5% shellac 15% plastic 8-10% plastic, with castor oil		J. Moores & Co., Salford, England	BP, 1931, 2, 444; Plastics, 1929, 5, 156; CM-4
<b>Micarta</b> (Mikarta)	PF, UF	l, ware	Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.	AR355; CM-4
<b>Mico</b>		Insulators	Mogadore Insulator Co., Mogadore, Ohio	PGB-1
<b>Micolite</b>	PF, glitens	m	E. H. Kellogg & Co., Paris; Paul Edgard Basset, Paris	CM-4
<b>Milusite</b>	PF			Rev. gen. de l'elect., 1926, 19, 624
<b>Minotext</b>	PF, asbestos filler	m		CM-4
<b>Miscbol</b>	Potassium oleo-abietae		Glyco Products Co., Inc., Brooklyn, N. Y.	
<b>Mold Wood</b>		Wood substitute	Wood Amalgam Co., Bloomfield, N. J.	BPY
<b>Moldarta</b>	PF, UF	m	Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.	CM-4
<b>Moldite</b>	CA		American Cellulose & Chemical Mfg. Co., New York	CM-4
<b>Monolite</b> (Monolithe)	X	Hot molding	Monowatt Electric Corp., New York; General Electric Co., Pittsfield, Mass.	PGB-3; CM-4; K-3
<b>Mouldenatte</b>	PF	m	Damard Lacquer Co., Greet, England; Rakelite Ltd., London, S.W. 1	CM-4; BPY
<b>Mouldings of Merit</b>	F, PF, UF	Articles	Insulators, Ltd., London, N. 18	CM-4; BPY
<b>Mouldrite</b>	F, PF	m, s	Croydon Mouldrite, Ltd., Croydon, England	CM-4; BPY

Name	Composition	Forms, Uses	Company	Source
<b>Mowilith</b>	Vinyl resins	Coatings, adhesives, plastics	Advance Solvents & Chemical Co., New York; I. G. Farbenind. A.-G., Frankfurt, Germany	APV-1, 3; K-3; CM-4
<b>Mowital</b>	Polysacetal		I. G. Farbenind. A.-G., Frankfurt, Germany	
<b>Mycalex</b>	Mica-lead borate	m	General Electric Co., Schenectady, N. Y.; Isolantite, Inc., Belleville, N. J.	BP, 1933, 4, 341; CM-4
<b>Myrac</b>	PF, liquid		Mitchell-Rand Mfg. Co., New York	
<b>N. A. D.</b> (N. A. F.)	Ebonite		McLeod & McLeod, London, W.C. 1	K-6
<b>N. P. S. Resin</b>	Cumarone-Indene	s, oil varnishes and chewing gum	Neville Co., Pittsburgh, Pa.	APV-3
<b>Nacrolaque</b>	CA	Pearl sheeting	May & Baker, Ltd., London, S.W. 11; Jos. H. Meyer Bros., Brooklyn, N. Y.	BPY; CM-4; PGB-2
<b>Nally Ware</b>	?SR	Ware	Nally, Ltd., Sidney, N.S.W., Australia	BPY
<b>Nameloid</b>	CA base	Imitation silver	Harrold Mfg. Co., Ltd., Birmingham, England	CM-4; BPY
<b>Necolastic</b>		Cements	Imperial Chem. Industries, London, S.W. 1	CM-4
<b>Neillite</b>	UF	m	Watertown Mfg. Co., Watertown, Conn.	PGB-3, CM-4
<b>Neoleukorit</b>	PF		U. S. S. R.	CM-4
<b>Neolith</b> (Neolite)	PF	l		Plastics, 1930, 6, 705; CM-1; AR355
<b>Neolitha</b>	C		Deutsche Kunsthorn-G.m.b.H., Harpburg-Hamburg, Germany	KPM283; CM-4
<b>Neophan</b>	CA	P	Cellon Works, Charlottenburg, Berlin	KPM283; CM-4; PGB-2
<b>Neorenit</b>	PF	s, m	Aug. Nowack A.-G., Bautzen, Germany	CM-4; APV-2
<b>Nestorite</b>	PF	m, s	James Ferguson & Sons, Ltd., Merton Abbey, London; Mica & Insulating Supplies Ltd., Melbourne, Victoria, Australia	CM-4; BPY
<b>Neville Resin</b>	Cumarone-Indene	Coatings, plastics	Neville Co., Pittsburgh, Pa.	PGB-3; APV-3; CM-4
<b>Nevindene</b>	Cumarone-Indene	Coatings	Neville Co., Pittsburgh, Pa.	APV-3
<b>Nibren Wax</b>	Halogenated naphthalenes		Advance Solvents & Chemical Corp., New York	
<b>Nilerodium</b>	PF, bitumen	Molded articles	Pritchett & Gold and E. P. S. Co., London	BP, 1934, 6, 317
<b>Nixinoid</b>	Gelatin products		H. Bossi	KPM284; CM-4
<b>Nixonoid</b>	Px		Nixon Nitration Works, New Brunswick, N. J.	PGB-1; CM-4
<b>Nobeline</b>	PF	t	Sicaloid, Ltd., London, E.C. 4; Soc. Nobel Francaise, Paris	CM-4; BPY; K-3
<b>Norgine</b>	X, alginates		Chem. Fabr. Norgine, Aussig, Germany	Plastics, 1930, 6, 656; CM-4
<b>Norloc</b>	F	m	Norton Labs. Co., Lookport, N. Y.	CM-4
<b>Nosplita</b>	Transparent and translucent resins	f	Ambi-Verwaltung, Berlin-Johannesthal	K-5; CM-4

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Name	Composition	Forms, Uses	Company	Source
<b>Noveloid</b>	Products from cellulose esters and ethers		Imperial Chem. Industries, Ltd London, S.W. 1	CM-4
<b>Novite</b>	PF	m	Imperial Chem. Industries, Ltd., London, S.W. 1	CM-4
<b>Novolak</b>	PF Also general term for fusible soluble PF resins made with acid catalyst Includes class known as "Saliretin" resins.	s	Bakelite Corp., New York	APV-2; NSR124; CM-4; AR146
<b>Novollithe</b>	CA		Soc. Bellignite, Bellignat, France	K-1; CM-4
<b>Novoresalt</b>	Resorcinol- Trioxymethylene		Aug. Nowack, Bautzen, Germany	APV-2; CM-4; K-3
<b>Novotext</b>	PF	Molded gears (fabric filled)	Germany	Plastics, 1930, 6, 705; CM-4
<b>Nuloid</b>	PF	s	U. S. A.	NSR118; KPM284
<b>Nuplax</b>	UF	m	American Nuplax Corp., New York	CM-4; PGB-3
<b>Nusal</b>	PF, F		Williams & Laird, Methil, Scotland	CM-4
<b>Oil Stop</b>	Liquid cashew- shell polymer	Used with para- form for cable splices	Irvington Varnish & Insulator Co., Irvington, N. J.	
<b>Olovine</b>	Polyvinyl esters condensed with extracted "stand oil," such as Tekaoil (q.v.). See also Chapter 61 of text.			Chem. Abs., 1932, 26, 606
<b>Omegite</b>	PF	m	Brit. Dyestuffs Corp., Ltd., (I.C.I.), Manchester, England	K-5; CM-4
<b>Omnillithe</b>	C		Motende, Charente, France	PGB-2; K-1; CM-4
<b>Onazote</b>	?	Heat insulation		BP, 1930, 2, 242; CM-4
<b>Ondoine</b>	PF	m	Soc. anon. Franc. du Ferodo, Paris	CM-4
<b>Ondolta</b>	PF	m	Afcom, Ltd., London; Soc. anon. Franc. du Ferodo, Paris	CM-4; BPY
<b>One Bake</b>	SR	Coating	Nobel Chemical Finishes, Ltd., Slough, England	K-6
<b>Opal</b> See Ivolt	PF	t		K-3; CM-4
<b>Opalax</b>		Non-explosive celluloid articles	Crayonne, Ltd., Bexley, Kent, England	KPM284; CM-4; BPY
<b>Orca</b>	Acrolein resin	Insulation and lacquers	France	NSR116, 164
<b>Oriak</b>	PF, F		Chance Bros. & Co., West Smethwick, England	CM-4
<b>Ornalth</b>	PF	t	Herold, A.-G., Hamburg, Germany	CM-4
<b>Orolithe</b>	CA		Soc. l'Orolithe, Rueil, France; Soc. l'Oyonnaxienne, Oyonnax, France	APV-2; CM-4
<b>Ortolan</b>		Insulation	Gebr. Mayer, Esslingen, Germany	CM-4
<b>Ostolit</b>	PF	m, s	Ostolit Corp., Winchester, Mass.	PGB-3; CM-4
<b>Oyocetyl</b>	CA		Soc. l'Oyonnaxienne, Oyonnax, France	APV-2; CM-4
<b>P.X.</b>	Ebonite		McLeod & McLeod, London, 117, 118	K-6

Name	Composition	Forms, Uses	Company	Source
<b>Panalac</b>	Shellac		Kasebier-Chatfield Shellac Co., New York	PGB-1
<b>Pandura C</b>	PF	s	Paramet Chem. Corp., New York	J.S.C.I. 1934, 53, 613
<b>Panelyte</b>	PF	l	Panelyte Corp., Trenton, N. J.	PGB-3; CM-4
<b>Panilax</b>	Aniline-formaldehyde, with paper pulp	Insulating material	Micanite & Insulators Co., Ltd., London, E. 17	BP, 1933, 4, 551; CM-4
<b>Panohite</b>	?		I. Paenson & Cie., Paris	CM-4
<b>Panplastic</b>	PF	t	American Plastics Corp., New York	PGB-3; CM-4
<b>Pantolit</b>	PF	t	Augeburger Kunsthars-Fabrik, Augsburg, Germany; Punfield & Barstow, Ltd., London, E.C. 2	CM-4
<b>Panserglas</b> , German generic name for bullet-proof glass				CM-4
<b>Papier Mache</b>	W, pressed paper			CM-4
<b>Papyroplast</b>				BP, 1930, 2, 323; CM-4
<b>Paracoumarone</b>	Cumarone and/or indene resin		Barrett Co., New York	CM-4
<b>Paradura C</b>	PF	s, coatings	Paramet Chemical Corp., New York	APV-3
<b>Paragutta</b>	Rubber, wax	Electrical insulation	Bell Telephone Labs., New York	APV-2; CM-4
<b>Paralac</b>	GP&PF-SR	s, m	Imperial Chem. Industries, Ltd., London, S.W. 1	BPY; CM-4
<b>Paralithe</b>	D, ?		Établissements Kuhlmann, Paris	CM-4
<b>Paraloid</b>			Paraloid Works, Inc., New York	PGB-1
<b>Paramet Ester Gum</b>	Natural resin modified with glycerol	Coatings	Paramet Chemical Corp., New York	APV-3
<b>Paranol, 10, Hard, EX Hard</b>	PF	s	Paramet Chemical Corp., New York	APV-3; CM-4
<b>Paraplex 5B EGI, G70</b>	Alkyd resin		Resinous Products Co., Philadelphia, Pa.	APV-3
<b>Paravar</b>	Chlorinated rubber	s	Naugatuck Chem. Co., Naugatuck, Conn.	
<b>Parfalt</b>	Px	Dentures	Parisen Chem. Co., Toledo, Ohio	CM-4
<b>Parkesite (Parkesine)</b>	Px and rubber, with oils		Parkes, in England, 1865	K-1
<b>Paralimon</b>	SR		Ver. Stahlwerke, A.-G., Düsseldorf, Germany	CM-4
<b>Parosiac</b>	GP	s		CM-4
<b>Parcolin</b> See Fiber Diamond				KPM284
<b>Patentlack</b>	D	Hardenable binder	Louis Blumer, Zwickau, Germany	CM-4
<b>Paxolin</b>	PF	l, insulation	Micanite & Insulators Co. Ltd., London	Plastics, 1929, 5, 156; K-4; CM-4
<b>Pearloid</b>	Px		Jos. H. Meyer Bros., Brooklyn, N. Y.	PGB-2; CM-4
<b>Pennacol</b>	Coal-tar product		Pennsylvania Coal Products Co., Petrolia, Pa.	PGB-3

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Name	Composition	Forms, Uses	Company	Source
<b>Pensulate</b>		Insulating materials	Blackall Bros. Ltd., London, E. 15	CM-4
<b>Peralit</b> (Peralite)	PF	P, l		<i>Plastics</i> , 1930, 6, 705; CM-4; AR355
<b>Pergut</b>	Chlorinated rubber		Advance Solvents & Chem. Corp., New York	<i>Syn. App. Fin.</i> , 1934, 5, 83
<b>Permachrome</b>	GP			<i>Plastics</i> , 1933, 9, 232; CM-4
<b>Permall</b>	PF	a	Le Bois Bakelisé, Nancy, France	CM-4
<b>Permaplastic</b>	PF		E. M. Wright, London, E.C. 4	CM-4
<b>Perspex</b>	SR	m, f	Imperial Chem. Industries, London, S.W. 1	BP, 1935, 6, 440
<b>Pertinax</b>	PF		Meirowsky & Co., Pors am Rhein, Germany	CM-4
<b>Pertinit</b>	UF, F		Meirowsky & Co., Pors am Rhein, Germany	CM-4
<b>Petrex</b>	$\alpha$ -Terpinene-ma- leic anhydride		Hercules Powder Co., Wilmington, Del.	
<b>Phenac</b>	PF modified with ester gum		American Cyanamid and Chem- ical Corp., New York	<i>Ind. Eng. Chem.</i> , 1934, 26, 714, <i>Paint, Oil, Chem.</i> <i>Rev.</i> , 1935, 97 (17)
<b>Phenester</b>	SR, coumarone type		Neville Co., Pittsburgh, Pa.	CM-4
<b>Phenoform</b>	PF		U S.A.	NSR118
<b>Phenoid</b>	PF		Mica Mfg. Co., Ltd., England	CM-4
<b>Phenolic</b>	PF, F		American Record Corp., Scranton, Pa.	CM-1
<b>Phenolin</b>	PF	t	Du Pont Viscoloid Co., Arlington, N. J.	
<b>Phenolite</b>	PF, UF	l	National Vulcanized Fibre Co., Wilmington, Del.	PGB-3, CM-4
<b>Phenoplasts</b> See <b>Esiste</b>	PF			AR146; KPM285
<b>Philite</b>	PF	m	N. V. Philips Gloeilampenfab- riecken, Eindhoven Holland; Philips Industrial, London	K-4; CM-4; BPY
<b>Plexigum</b>	D	Used in Luglas	Röhm & Haas, A.-G. Darmstadt, Germany, and Philadelphia, Pa.	CM-4; PGB-3
<b>Phobophene</b>		From tannery waste	Westinghouse Electric & Mfg. Co., East Pittsburgh, Pa.	CM-4
<b>Phonycord</b>	Px, I, F	Records	Phonycord, G.m.b.H., Berlin	CM-4
<b>Piccin</b>	Bituminous	Flexible thermo- plastic cement	Schrader & Ehlers, New York	
<b>Plaskon</b>	UF	m	Toledo Synthetic Products, Inc., Toledo, Ohio	<i>Plastics</i> , 1931, 7, 664; BP, 1932, 3, 477; CM-4
<b>Plasmic</b>	SR		James Packer Wagner, London, E.C. 2	BP, 1934, 6, 180
<b>Plass</b>	UF	Organic glass t	Pollopas, Ltd., Nottingham, England	CM-4
<b>Plastacole</b>	CA	m, f	Du Pont Viscoloid Co., Arlington, N. J.	PGB-3; CM-4
<b>Plastam</b>	?		Soc. Lilloise Plastam, Lille, France	CM-4
<b>Plastico</b>	?		M. Marica, Vaucluse, France	RGP, 1930, 6, 509; CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Plasticon</b>	Non-drying adhesive, containing rubber derivative		B. F. Goodrich Rubber Co., Akron, Ohio	
<b>Plastine</b> (Plastin)	CA		Soc. Nobel Francaise, Paris; Sicaloid Ltd., London, E.C. 4	BPY; APV-2; PGB-2; CM-4
<b>Plasto Resin</b>	Polystyrene		Advance Solvents & Chemical Corp., New York	APV-3; CM-4
<b>Past-o-cerex</b>	SR		Rex Campbell & Co., Ltd., England	CM-4
<b>Plastopal</b>	UF	s	I. G. Farbenind. A.-G., Germany; Pollopas, Ltd., London, E.C. 1	<i>Syn. Appl. Fin.</i> , 1932, 7, 120; APV-2; CM-4
<b>Plastose</b>	PF, CA, F	m	Soc. la Plastose, Paris IX; Soc. Vandier, Niort France; Afcom, Ltd., London	PGB-2; CM-4, K-1
<b>Plax</b> See <b>Eucel</b>	Rubber-cellulose	s	Plax Products, Ltd., London, S.E. 5	APV-2; CM-4, BPY
<b>Flexite</b>	SG with SR interlayer		Rohm & Haas A.-G., Darmstadt, Germany	CM-4
<b>Phalite</b>	Rubber resins	s	Goodyear Tire & Rubber Co., Akron, Ohio	CM-4; PGB-3
<b>Plioform</b>	Rubber derivative	m	Goodyear Tire & Rubber Co., Akron, Ohio	CM-4; <i>Plastics</i> , 1933, 9, 18
<b>Pliolite</b>	Rubber derivative	s	Goodyear Tire & Rubber Co., Akron, Ohio	BP, 1933, 4, 545; APV-3
<b>Pluviusin</b>	UF		Kunstharzfabrik Dr. F. Pollak, Vienna	CM-2
<b>Plynalith</b>			Isaac Frenkel, Paris	PGB-2
<b>Pollopas</b>	UF, F	m, s	Kunstharzfabrik Dr. F. Pollak, Vienna; Dynamit A.-G., Troisdorf, Germany; Etablissements Kuhlmann, Paris	CM-4
<b>Pollopas-Platten</b>	UF	l	Venditor, G.m.b.H., Berlin	CM-2
<b>Polynit</b>	Polymerized butadiene		I. G. Farbenind. A.-G., Frankfurt, Germany	
<b>Polyroc</b>	?	t	Etablissements Kuhlmann, Paris	CM-4
<b>Polysti</b>	Px		I. G. Farbenind. A.-G., Frankfurt, Germany	K-5
<b>Porcedent</b>	Vinyl (?)	Denture		CM-4
<b>Porcellanite</b> (Porsellanite)	C		Soc. de Carraud, Ruel, France	K-1; KPM286; PGB-2
<b>Press Mass</b>			American British Chemical Supplies, Inc., New York	PGB-2
<b>Pressmikanit</b> (Press Micanite)	PF-mica	l		<i>Plastics</i> , 1930, 6, 705; CM-4; AR355
<b>Presssell</b>	PF			<i>Plastics</i> , 1930, 6, 705; CM-4
<b>Prestellan</b>	Resins		Allgem. Elektrizitäts-Ges., Berlin	CM-4
<b>Prestonit</b>	Asbestos and binder			CM-4; KPM286
<b>Pressspan</b>	Gelatinized cellulose			KPM286
<b>Priscal</b>	UF	t	Soc. anon. des Matières Plastiques, Paris	CM-4



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Name	Composition	Forms, Uses	Company	Source
<b>Prisma</b>	? F	Ware	Mica Mfg. Co., Ltd., Bromley, Kent, England	CM-4; BPY
<b>Probe</b>	PF, F	l	L. Poulain, St. Ouen, France	CM-4
<b>Progilac</b>	Cellulose-base varnishes	Acid- and alkali-resistant	Soc. Résines & Vernis Artificiels, Paris	CM-4; BPY
<b>Progilite</b>	PF	s, m	Soc. Progilite, Lyons, France; Soc. Résines & Vernis Artificiels, Paris	APV-2; PGB-1; BPY; K-4
<b>Protectoid</b>	CA	P	Celluloid Corp., Newark, N. J.	CM-4
<b>Proteolite</b>	C		Industria Italiana della Proteolite, Milan, Italy	PGB-2; CM-4
<b>Prystal</b>	UF	t	Sicaloid, Ltd., London; Soc. Industrielle des Matières Plastiques, Paris	BP, 1931, 2, 552; KPM286; CM-4
<b>Prystalline</b>	UF	m	Soc. Nobel Francaise, Paris	CM-4
<b>Pyradolite</b>	Px	f	Du Pont Viscoloid Co., Arlington, N. J.	PGB-3; CM-4
<b>Pyralin</b>	Px		Du Pont Viscoloid Co., Arlington, N. J.; Canadian Industries, Ltd., Montreal, Quebec	CM-4
<b>Pyrido Rubber</b>	Polymerized acrolein-methylamine			AR128
<b>Pyroplax</b>	PF, X	Cold molding	Cutler-Hammer, Inc., Milwaukee, Wis.	CM-4
<b>Pyroxote</b>	Px solution		Pyroxilin Products, Inc., Chicago, Ill.	PGB-3
<b>R. P. X.</b>	Ebonite sheets		McLeod & McLeod, London, W.C. 1	K-6
<b>Radifix</b>	Rapeseed oil-sulphur chloride product			Chem. Abs., 1931, 25, 6016
<b>Radionite</b>	SR			KPM286; CM-4
<b>Rainbow Ware</b>	UF, F		Billmyre Mfg Co., Ltd., London, S.E. 17	CM-4
<b>Ramos</b>	PF, F		Universal Electric Lamp Co., London, E.C. 2	CM-4
<b>Redionite</b>	Copal		Soc. Francaise, Gardy, France	K-1; PGB-2
<b>Redmanol</b>	PF	m	Bakelite Corp., New York; Bakelite, Ltd., London, S.W. 1	CM-4; BPY
<b>Redlite</b>	SR	m	Dante Badino, Genoa, Italy	CM-4
<b>Reicolit</b>		Insulation	Reicolit G m.b.H., Berlin	CM-4
<b>Reliance</b>	Px and CA, F		Reliance Ltd., Twickenham, England	CM-4; K-4
<b>Replit</b>	PF			CM-4
<b>Repetit (Repetite)</b>	PF			Plastics, 1930, 6, 705; CM-4; AR355
<b>Resan</b>	PF	t	Bakelite Corp., New York; Kunstharfabrik Resan, Mosbierbaum, Germany	NSR113, 179; CM-4; K-1
<b>Resanit</b>	PF	t	Kunstharfabrik Resan, Mosbierbaum, Germany	CM-4
<b>Rescolite</b>	PF	m, s	Rescolite Corp., Newtonville, Mass.	PGB-3; CM-4
<b>Resonoplast</b>	GP			APV-2

Name	Composition	Forms, Uses	Company	Source
<b>Resibond</b>	SR, paper	Used to bond plywood	Bakelite Ltd., London, S.W. 1	BP, 1934, 6, 272
<b>Resifilm</b>	SR, paper	Used to surface wood	Bakelite, Ltd., London, S.W. 1	BP, 1934, 6, 272
<b>Resin AH, AW 1, AW 2</b>	SR	s	Advance Solvents & Chem. Corp., New York; J. M. Steel & Co., Ltd., London, W.C. 2	CGP, 1931, 28, 15, 366; CM-4, APV-2
<b>Resin KM</b>	Modified alkyd resin		Advance Solvents & Chem. Corp., New York	CM-4
<b>Resin TC</b>	SR	s, adhesive with ethyl cellulose	Advance Solvents & Chem. Corp., New York; J. M. Steel & Co., Ltd., London, W.C. 2	BPY
<b>Resin Superba</b>	PF		Italy	Plastics, 1929, 5, 38; CM-4
<b>Resin Superbo</b>	PF		Italy	Plastics, 1929, 5, 38; CM-4
<b>Resin 26-M</b>	SR	Compatible with CA, nitrocellulose and vinyl acetates	Advance Solvents & Chem. Corp., New York	APV-3
<b>Resinit (Resinite)</b>	PF	s, t	Bakelite G.m.b.H., Germany; Knoll & Co., Ludwigshafen, Germany	PGB-2, APV-2; CM-4
<b>Resinoid</b>	F		Établ. Durrachmidt, Lyons, France	CM-4
<b>Resinol</b>	PF	s, m	Dr. F. Raschig G.m.b.H., Ludwigshafen, Germany	CM-4; APV-2; Cf. NSR11
<b>Resinoplast</b>	SR	Plasticiser		Chem. Abs., 1931, 25, 423
<b>Resinox</b>	PF	s, m	Resinox Corp., New York	CM-4; APV-2
<b>Resistan</b>	PF	Heat-resisting	Kontakt-Römmeler A.-G., Frankfurt, Germany	CM-4
<b>Resisto</b>		Insulation	Tuco Products Corp., New York	PGB-1
<b>Resitol</b>				Plastics, 1929, 5, 531
<b>Resiston</b>		Hard rubber insulation		Plastics, 1929, 5, 531
<b>Resit (Resite)</b>	Cf. Resol, Resitol and Phenoplast Collective name for PF resins in the "C" stage			NSR124; CM-4; Chem. Abs., 1933, 27, 3835; KPM287; AR146; Kunst., 1933, 23, 100; Chem. Ztg., 1913, 37, 734
<b>Resitol</b> , general name for the "B" stage of PF resins				NSR124; Chem. Ztg., 1913, 37, 734
<b>Resoglas (Resoglas)</b>	Polystyrene	s	Advance Solvents & Chem. Corp., New York	APV-3; CM-4
<b>Resoid</b> , general name for all resinous plastics, chosen in 1929, by N. E. M. A., Molded Insulation Section, but not generally adopted				Plastics, 1929, 5, 222
<b>Resol (Resole)</b> , general name for the soluble or "A" stage of PF resins				Chem. Ztg., 1913, 37, 734; NSR124; CM-4; KPM287
<b>Resolit</b>	Rubber composition			Plastics, 1929, 5, 531
<b>Resopal</b>	UF	m	H. Roemmler, A.-G., Spremberg, Germany	BP, 1931, 2, 148; CM-4

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Name	Composition	Forms, Uses	Company	Source
<b>Resopon</b>			Reso Products Co.	<i>Plastics</i> , 1929, 5, 531
<b>Resovin</b>	Vinyl resin	Dentures	S. S. White Dental Mfg. Co., Philadelphia, Pa.	BP, 1933, 5, 79; CM-4
<b>Resphan</b>			Reso Products Co.	<i>Plastics</i> , 1929, 5, 531
<b>Revolite</b>	Cloth impregnated with PF		Revolite Corp., New Brunswick, N. J.	CM-4; <i>Plastics</i> , 1933; 9, 21
<b>Reynolite</b>	F, SR		Reynolds Spring Co., Jackson, Mich.	CM-4
<b>Reynomold</b>	?	Articles	Reynolds Spring Co., Jackson, Mich.	BPY
<b>Reselite</b>	PF		Cussons Sons & Co., Manchester, England	CM-4
<b>Resinel</b>	Polymerized terpene resins		Glyco Products Co., Inc., Brooklyn, N. Y.	CM-4
<b>Resyl</b>	Alkyd resins	Coatings plasticisers	American Cyanamid & Chemical Corp., New York	APV-3; CM-4
<b>Rhodialine</b>	CA	P	Soc. des Usines Chim. Rhone-Poulenc, Paris; May & Baker, Ltd., London, S.W. 11	CM-4
<b>Rhodoid</b>	CA	f, m	Soc. des Usines Chim. Rhone-Poulenc, Paris; May & Baker, Ltd., London, S.W. 11; Canadian Industries, Ltd., Montreal	BPY; CM-4
<b>Rhodophane</b>	CA	P	Soc. des Usines Chim. Rhone-Poulenc, Paris; May & Baker, Ltd., London, S.W. 11	CM-4
<b>Richelain</b>	UF, F	Ware	Richardson Co., Melrose Park, Ill.	CM-4
<b>Richware</b>	PF	m	Makalot Corp., Boston, Mass.	PGB-3; CM-4
<b>Ricollit</b> (Ricollite)	PF		Sadd Isolatorenwerke, Freiburg, Germany	AR247; CM-4; BPY
<b>Ripolin</b>	?			RGP, 1932, 8, 319; CM-4
<b>Roanoid</b>	UF, F	m	Roanoid, Ltd., Glasgow, Scotland	CM-4
<b>Robert Rauh X-135</b>	Alkyd	s, varnishes	Robert Rauh, Inc., Newark, N. J.	APV-3
<b>Robert Rauh N-2, QD No. 1</b>	PF	s, varnishes	Robert Rauh, Inc., Newark, N. J.	APV-3
<b>Robert Rauh QDK</b>	PF and fossil resin	s, varnishes	Robert Rauh, Inc., Newark, N. J.	APV-3
<b>Roburine</b>	?, natural resin base	m	Soc. d'Isolants et Objets Moulés, Vitry, France	BPY; CM-4
<b>Rockite</b>	PF	s, m	Rockhard Resins, Ltd., London; F. A. Hughes & Co., Ltd., London, N.W. 1	CM-4; APV-2
<b>Rockshell</b>	PF	s, m	Rockhard Resins, Ltd., London	CM-4; APV-2
<b>Rocrex</b>	SR	s	Rex Campbell & Co., Ltd., England	CM-4
<b>Rollistic</b>	F, UF		Rolls Razor, Ltd., London, N.W. 2	CM-4; BPY
<b>Romalite</b>	Rubber resin product		Soc. La Ronite, Rosny, France	K-4; CM-4; KPM287
<b>Ronilac</b>	UF	For injection molding	Soc. La Ronite, Rosny, France	BP, 1931, 2, 574; CM-4; <i>Plastics</i> , 1932, 8, 239

Name	Composition	Forms, Uses	Company	Source
<b>Ronisol</b>	PF	For injection molding	Soc. La Ronite, Rosny, France	BP, 1931, 2, 574; CM-4; <i>Plastics</i> , 1932, 8, 239
<b>Ronite</b>	CA	For injection molding	Soc. La Ronite, Rosny, France	CM-4
<b>Ronyx</b>	PF	f, t		<i>Modern Plastics</i> , 1935, 19(9), 54
<b>Rouges Phobophene</b>	Tannery waste plastic			KPM287
<b>Roxon</b>	PF, F		Roxon, Ltd., London, E.C. 4	CM-4
<b>Rucel</b> See <b>Plax</b>	D, rubber-cellulose mixture	s	Plax Products, Ltd., London, S.E. 5	CM-4; BPY
<b>Rudex</b>	PF		Soc. Dorex, Paris	K-1; CM-4
<b>Runerit</b>	PF	l, m	Electro-Isolier-Industrie, Wahn, Germany	CM-4
<b>Ryterex</b>	PF		Jos. T. Ryerson & Son, Inc., Chicago	CM-4
<b>S.D.O.</b>	Synthetic drying oil from acetylene	Coating	E. I. du Pont de Nemours & Co., Wilmington, Del.	
<b>St. Bernard</b>	F, non-explosive cellulose deriv.	Molded articles	A. W. Kanis, London	KPM287, CM-4
<b>Sakaloid</b>	X, from sugar		Industrial Sugar Products Corp., New York	CM-4
<b>Saligenin</b> Type Resin, general name for PF resins made through the formation of saligenin (orthohydroxybenzyl alcohol) and its later transformations. Such resins are also known as "Saliretin" resins.				NSR127, 132; AR147
<b>Saliretin</b> , general term for PF resins such as those hardened by elimination of phenol from a Novolak type resin. Saligenin is formed at one stage in the process.				NSR124, AR146
<b>Sani-Jold</b>			Louis Samets, Inc., Westport, Conn.	PGB-1
<b>Santolite</b> <b>MHF, MS</b>	Toluene-sulphonamide-formaldehyde	Coatings	Monsanto Chemical Co., St. Louis, Mo.	APV-1, 2
<b>Satolite</b>	CA		Dr. Sato, Japan	K-1; PGB-2
<b>Scarab</b>	UF	m	Beetle Products Co., Ltd., London, W. 1	BP, 1934, 6, 167
<b>Scheel Lac</b>		Shellac substitute	Wm. H. Scheel, New York	PGB-1
<b>Shellan</b> (Shellan)	UF	s	Kunstharsfabrik Dr. F. Pollak, Vienna	APV-2; CM-4
<b>Shellit</b> (Shellit)	PF	t	Kunstharsfabrik, Dr. F. Pollak, Vienna; Établissements Kuhlmann, Paris	CM-4
<b>Seekay</b>	Chlorinated naphthalene		Imp. Chem. Ind., Ltd., England	<i>Chem. Age (London)</i> , 1934, 31, 383; CM-4
<b>Selenite</b>	C		England	K-1; PGB-2
<b>Sétabonite</b>	Rubber and resin		Mfrs. d'Isolants & Objets Moulés, Vitry, France	CM-4; K-4
<b>Sétacégélite</b>	PF	m	Mfrs. d'Isolants & Objets Moulés, Vitry, France	K-4; CM-4
<b>Bextol Stearate</b>	Methylcyclohexanol stearate	Plasticizer and mold lubricant	Howards & Sons, Ltd., Ilford, England	BP, 1933, 4, 452; BPY
<b>Shellold</b>			G. H. Harris Co., Brooklyn, N. Y.	PGB-1

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Name	Composition	Forms, Uses	Company	Source
<b>Shellware</b>	?	Articles	Gen. Mouldings Co., Ltd., London, N.W. 1; Brownie Wireless Co. (Great Britain), Ltd., London, N.W. 1	CM-4; BPY
<b>Sibolite</b>	PF	Shellac subst.	U.S.A.	AR283; CM-4; NSR118, 124
<b>Sicalite</b> (Sicalithe Sicalite N)	C, with resins or Px	f	Sicaloid, Ltd., London; Soc. Nobel Francaise, London; Soc. Industrielle du Celluloide, Paris	KPM287; CM-4; K-4
<b>Sicoid</b>	CA		Sicaloid, Ltd., London; Soc. Ind. du Celluloide, Paris	CM-4
<b>Sidac</b> <b>Sidac-Isol</b>	V	P	Sylvania Industrial Corp., Fredericksburg, Va.; Société Ind. de la Cellulose, Ghent, France	CM-4; K-4
<b>Sigaleos</b>	PF		Italy	Plastics, 1930, 6, 589; CM-4
<b>Similex</b>	PF	t	Labs. Ind. d'Asnières, Paris	CM-4
<b>Similit</b>	PF	t	Labs. Ind. d'Asnières, Paris	CM-4
<b>Stipilite</b> <b>Bakelit A</b>	PF	s		KPM288; AR324; CM-4
<b>Solidite</b>	SR, pitch and asbestos, F	m	Solidite & Synthetic Mouldings, Ltd, London, S.W. 4	CM-4; BPY
<b>Soligen</b>	Naphthenates of lead, cobalt, manganese	Paint driers	Advance Solvents & Chem. Corp., New York	
<b>Solith</b>	PF	t	Rejal & Spol, Prag, Czechoslovakia	CM-4
<b>Souvelo</b>	F, UF, ?	Ware	Souvenir Mfg. Co., Birmingham, England	CM-4
<b>Spaulding</b>	Bakelite F		Spaulding Fibre Co., Tonawanda, N. Y.	PGB-1
<b>Spauldite</b>	PF	l, gears	Spaulding Fibre Co., Tonawanda, N. Y.	CM-4
<b>Stabilite</b> Also called <b>Ambroline</b>	Copal-fiber		Soc. Grandgener, Perreux, France	Plastics, 1926, 2, 123; CM-1
<b>Stabilite Fine</b>	Rubber base di- electric and SR		Manufacture d'Isolants et Objets Moulés, Vitry, France	K-4; CM-4; BPY
<b>Stabstit</b>	SR		Soc. Grandseigneur, Perreux, France	K-4
<b>Stacol</b>	Inorganic sol- uble resin		Glyco Products Co, Inc, Brooklyn, N. Y.	CM-4
<b>Stanolite</b> <b>Liquid, Hard</b>	Petroleum resid- ual pitch	Plastics	Standard Oil Co of Indiana, Chicago	
<b>Starkware</b>	UF, F	Ware	Insulation Mfg. Co., Brooklyn, N. Y.	PGB-3; CM-4
<b>Starlite</b>	SR		Soc. Gén. Const. Electro-mechanique, Limoges, France	CM-4
<b>Starpass</b>	UF		Soc. Gén. Const. Electro-mechanique, Limoges, France	CM-4
<b>Stoco</b>	Bituminous plastic		Jos. Stokes Rubber Co., Ltd., Welland, Ontario, and Trenton, N. J.	PGB-3; CM-4
<b>Streetly</b>	UF, F	Ware	Streetly Mfg. Co., Ltd., London	CM-4
<b>Stryoflex</b>	SR	f	N. D. Seekabelwerke A.-G., Oldenburg, Germany	BP, 1934, 6, 179
<b>Su-Lac</b>		Substitute for shellac	Twin City Shellac Co., Brooklyn, N. Y.	PGB-1

Name Suberit	Composition Waste cork particles treated with collodion and castor oil	Forms, Uses	Company	Source CM-4; KPM288
<b>Super-Beckacite</b>	PF	s	Beck, Koller & Co., Inc., Detroit, Mich., and Vienna	CM-4
<b>Super-Micanite</b>	Glyptal-bonded mica		General Electric Co., Schenectady, N. Y.	APV-2; CM-4; BP, 1931, 3, 444
<b>Superisolite</b>	PF		Italy	Plastics, 1930, 6, 587; CM-4
<b>Superlit</b>	SR		Stein, Berlin	CM-4
<b>Suprarenen</b>	Dammar derivative	Paint vehicle		Brit. Chem. Abs. B, 1931, 768
<b>Sylphrap</b>	CA	P	Sylvania Industrial Corp., Fredericksburg, Va.	CM-4
<b>Sylraph</b>	V	P	Sylvania Industrial Corp., Fredericksburg, Va.	BP, 1931, 3, 149
<b>Sylvania</b>	V	P	Sylvania Industrial Corp., Fredericksburg, Va.	CM-4
<b>Syn-phorm</b>	SR		Blackburn & Oliver, England	K-4; CM-4; APV-2
<b>Synobel</b>		Cements	Imperial Chem. Industries, London, S.W. 1	CM-4
<b>Syntellac</b>	Acetaldehyde condensate	Shellac substitute	Roessler & Hasslacher Chem. Div., E. I. du Pont de Nemours & Co., Wilmington, Del.	AR260
<b>Synthaform</b>	PF, F		Synthaform, Berlin	CM-4
<b>Synthane</b>	PF	l	Synthane Corp., Oaks, Pa.	CM-4
<b>Synthe-Copal</b>	Ester gum	s	Beck, Koller & Co., Inc., Detroit, Mich.	PGB-1
<b>Syntholite</b>	PF?		Soc. anon. la Syntholite, Paris	K-4, CM-4
<b>T C Resin. See Resin, T C</b>				
<b>Tapa</b>	SR	Molded articles	W. J. Charlesworth, Ltd., Birmingham, England	CM-4; BPY
<b>Taumatit</b>	PF	t, f, ware	Condrup, Ltd., London, E.C. 2, Isopresswerk, Berlin	CM-4; BPY
<b>Taylor</b>	PF	l	Taylor & Co., Inc., Norristown, Pa.	CM-4; PGB-3
<b>Tegit</b>			Garfield Mfg. Co., Garfield, N. J.	PGB-1
<b>Teglac</b>	Modified GP	Lacquers	American Cyanamid & Chemical Corp., New York	APV-2, 3; CM-4
<b>Tego</b>	SR	s, adhesives	Th. Goldschmidt A.-G., Essen, Germany; Theo. Goldschmidt Corp., New York	CM-4; APV-2
<b>Tegofan</b>	Chlorinated rubber		Th. Goldschmidt, A.-G., Essen, Germany; Tegofan G.m.b.H., Hamburg, Germany	CM-4
<b>Tegopren</b>	SR		Th. Goldschmidt, A.-G., Essen, Germany	CM-4
<b>Teknol</b>	The mixture of unsaturated glycerides separated from the saturated glycerides in stand oil, or specially treated drying oils			
<b>Telac</b>	F?	Molded articles	J. H. Tucker & Co., Ltd., Birmingham, England	BPY

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Name	Composition	Forms, Uses	Company	Source
<b>Telacite</b>	PF	m	J. H. Tucker & Co., Ltd., Birmingham, England	BPY; AR347
<b>Telconax</b>	Bituminous plastic		Telegraph Const. & Maintenance Co., London	CM-4
<b>Telconite</b>		Insulation	Telegraph Const. & Maintenance Co., London	CM-3
<b>Telenduron</b>	?	m, insulators	Thomas de la Rue & Co., Ltd., London	CM-4
<b>Tenacite</b> (Tenaosit Tenasit)	F, asbestos-bituminous PF	m	Allgem. Elektr. Ges., Berlin	PGB-2; K-1; CM-4; KPM288
<b>Tenalan</b>	PF	f		Plastics, 1930, 6, 705; CM-4; AR347
<b>Tenatext</b>	PF, rag-filled	m	Allgem. Elektr. Ges., Berlin	CM-4
<b>Tenarit</b> See Textolite	PF		Allgem. Elektr. Ges., Berlin	CM-4
<b>Tenite</b>	CA	m, f	Tennessee Eastman Corp., Kingsport, Tenn.	CM-4
<b>Tensulam</b>	Thermoplastic	Acid- and alkali-resisting, m	Berry, Wiggins & Co., Ltd., England	BPY; CM-4; KPM288
<b>Tepperite</b>	Polystyrene	Denture	Martin Rubber Co. & Tepperite Co., Long Island City, N. Y.	CM-4; PGB-3
<b>Tetrolith</b>	?		Kunstthornwerke Teterow, Mecklenburg, Germany	CM-4
<b>Text-Tiles</b>	UF?	Tiles	Kelacoma, Ltd., Welwyn, Garden City, England	CM-4, K-4
<b>Textit</b>	F	Acid-proof moldings	Cable Mfg. Co. Ltd., England; Kabel-Fabrik A.-G., Bratislava, Czechoslovakia	CM-4; BPY
<b>Textodite</b>		Timing gears	John C. Hoof & Co., Chicago	PGB-1
<b>Textoll</b>		Fiber gear board	General Electric Co., Schenectady, N. Y.	PGB-1
<b>Textolite</b>	PF	f, m, l	General Electric Co., Schenectady, N. Y.	CM-4
<b>Thermasote</b>	W		Agasote Millboard Co., Trenton, N. J.	CM-4; K-4
<b>Thermold</b>		Cold molding	Technical Products Co., Pittsburgh, Pa.	PGB-1
<b>Thermolite</b>	Px	Denture	Thermolite Prod. Corp., Chicago	PGB-2
<b>Thermoplax</b>	X	Cold molding	Cutler-Hammer, Inc., Milwaukee, Wis.	CM-4
<b>Thermoprene</b>	Rubber derivative	Adhesive	B. F. Goodrich Rubber Co., Akron, Ohio	
<b>Thermose</b>	CA, benzyl cellulose	Dentures	"Bakelite" Dental Supplies, London, N. 3	CM-4; BPY
<b>Theait Supra</b>	SR	m	Presswerk A.-G., Essen, Germany	CM-4; K-6
<b>Theait Textil</b>	SR	l	Presswerk A.-G., Essen, Germany	CM-4; K-5
<b>Thickol</b>	Polymethylene polysulphide			BP, 1933, 4, 440; CM-4
<b>Thiobonite</b> See Thiojectite	Ebonite SR	Alkali-resisting		BP, 1930, 2, 52; Plastics, 1931, 7, 19; CM-4
<b>Thiojectite</b>	Ebonite SR	Injection molding	Soc. la Thiolite, Joinville-le-Pont, France	Plastics, 1931, 7, 19; BP, 1930, 2, 52; CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Thiokol</b>	Olefin poly-sulphide	Molded articles rubber substitute	Thiokol Corp., Yardville, N. J.	BP, 1933, 4, 440; CM-4
<b>Thiolite</b>	PF treated with sulphur chloride		Soc. la Thiolite, Joinville-le-Pont, France	J.S.C.I., 1927, 48, 573; CM-4
<b>Thyrite</b>	Porcelain type plastic, silicon carbide coated with metal, by spray process	Lightning ar- resters	General Electric Co., Schenectady, N. Y.	Ind. Eng. Chem., 1930, 22, 395; CM-4
<b>Tornesite</b> (Tornesit)	Chlorinated rubber	Coating	Hercules Powder Co., Wilmington, Del.; Herold A.-G., Hamburg, Germany	Syn. App. Fin., 1931, 3, 89; J85; CM-4; Chem. Abs., 1933, 27, 2337
<b>Toron</b>	Turpentine- sulphur	Impregnant		
<b>Tortaloid</b>	CA, F		Fiberloid Corp., Indian Orchard, Mass	APV-2; CM-4
<b>Totalite</b>	C	Whitener for in- terior walls	Wilbur & Williams Co., 101 Park Ave., N. Y. C.	Plastics, 1933, 9, 252
<b>Transperit</b> (Transparit)	V	P	Wolff & Co., Walsrode, Germany	PGB-2; CM-4; KPM289
<b>Transphillite</b>	?	f, m	Philips Industrial, London, W.C. 2; N. V. Philips' Gloeilampenfabrieken, Eindhoven, Holland	BPY
<b>Trefoil</b>	PF		Bakelite, Ltd., London, S.W. 1	CM-4
<b>Trolit</b>	Px, CA	f, m, l	Rhen. Westf. Sprengstoff A.-G., Troisdorf, Germany; Adam Bernhard, New York	CM-1; K-4
<b>Trolit F</b>	Px	Non-inflammable	Dynamit A.-G., Troisdorf, Germany	CM-4
<b>Trolit S</b>	PF	m	Dynamit A.-G., Troisdorf, Germany	CM-3
<b>Trolit-Spezial</b>	PF	m	Dynamit A.-G., Troisdorf, Germany; Adam Bernhard, New York	CM-4; PGB-3
<b>Trolit W</b>	CA	m	Dynamit A.-G., Troisdorf, Germany	CM-4
<b>Trolitan</b>	PF	m, wood flour	Dynamit A.-G., Troisdorf, Germany; Adam Bernhard, New York	CM-4; PGB-3
<b>Trolitan H</b> Now called <b>Follopas</b>	UF	m	Dynamit A.-G., Troisdorf, Germany; Adam Bernhard, New York	CM-4; PGB-3
<b>Trolitan Profile</b>		Continuous molded shapes	Dynamit A.-G., Troisdorf, Germany	CM-4
<b>Trolitan S</b>	PF	m	I. G. Farbenind. A.-G., Troisdorf, Germany	
<b>Trolitan Z</b>	PF	m, light colors	Dynamit A.-G., Troisdorf, Germany	CM-4
<b>Trolitax</b>	PF	l	Adam Bernhard, New York; Dynamit A.-G., Troisdorf, Germany; F. A. Hughes & Co., Ltd., London, N.W. 1	CM-4; BPY
<b>Trolite</b>	Px	f	F. A. Hughes & Co., Ltd., London, N.W. 1	BPY; KPM289
<b>Trolite</b> <b>Special E</b>	UF			AR408
<b>Trolitul</b>	Polystyrene	m	Dynamit A.-G., Troisdorf, Germany; F. A. Hughes & Co., Ltd., London, N.W. 1	CM-4; BPY
<b>Trolitul-folien</b>	?		Dynamit A.-G., Troisdorf, Germany	CM-4



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Name	Composition	Forms, Uses	Company	Source
<b>Trolon</b>	PF	t	Dynamit A.-G., Troisdorf, Germany; Adam Bernhard, New York	CM-4; PGB-3
<b>Trolon-Platten</b>	PF	l, t	Dynamit A.-G., Troisdorf, Germany; Venditor G.m.b.H. Berlin	CM-4; K-5
<b>Trolone</b>	PF	t	F. A. Hughes & Co., Ltd., London, N.W. 1	BP, 1934, 6, 173
<b>Troluloid</b>	Vinyl resin		Dynamit A.-G., Troisdorf, Germany	CM-4
<b>Trubor</b>	SR, wood	Boards, sheets	Games & Entertainments Supply Co., Ltd., London	BP, 1934, 6, 86
<b>Tufnol</b> (Tufnal)	PF	l, f	Ellisqn Insulations, Ltd., Birmingham, England	K-4; CM-4
<b>Tuftest</b>	Vulcanized fiber	f	Wilmott, Son & Phillips, Ltd, London, E C. 3	BPY
<b>Turax</b>	PF	l		Plastics, 1930, 6, 705, CM-4 AR355
<b>Turbax</b>	PF	l	Jaroslav's Glimmer-Waren-Fabrik, Berlin	CM-4
<b>Turbonit</b> (Turbonite)	PF	m, l	Jaroslav's Glimmer-Waren-Fabrik, Berlin	CM-4; AR355
<b>Tylose</b>	Methyl cellulose ether	s	Advance Solvents & Chem. Corp., New York	APV-2; CM-4
<b>Ultrasit</b>	PF	t, l	Chemische Fabrik Ambrasit, Vienna; H. Ilner, London, E C. 1	CM-4; BPY
<b>Unyte</b>	UF	m	Unyte Corp., New York	CM-4; Plastics, 1932, 8, 76
<b>Uralite</b>	UF	m, f	American Record Corp, Scranton, Pa.; Soc. Résines & Vernis Artificiels, Paris	CM-4
<b>Ureft</b> (Ureite)	Collective name for UF resins			Chem. Abs., 1933, 27, 3835; CM-4; Kunst., 1933, 33, 100
<b>Urocristal</b>	UF	m, transparent	Soc. Résines & Vernis Artificiels, France	CM-4
<b>Urophane</b>	UF	m, transparent	Soc. Résines & Vernis Artificiels, Paris	CM-4
<b>Uthit</b> (Utileit)	PF	t	Augsburger Kunstharz-Fabrik, Augsburg, Germany	CM-4
<b>VGB</b>	Aniline-aldehyde condensation	Rubber antioxidant	Naugatuck Chem. Co., Naugatuck, Conn.	Chem. Abs., 1932, 26, 3408
<b>Vanalite</b>		m	Vitalite Co., Ltd., London	Plastics, 1929, 5, 156
<b>Varerex</b>	SR		Rex Campbell & Co., Ltd, England	CM-4
<b>Varcum</b>	PF	s	Varcum Chemical Corp., Niagara Falls, N. Y.	CM-4; PGB-3
<b>Varised Fibre</b>	Fiber board	Insulation	Sterling Fibre Board Co., New York	PGB-1
<b>Varnodag</b>	Colloidal graphite in PF varnish		Acheson Colloids Corp., Port Huron, Mich.	
<b>Veryx</b>	UF		Edgard Israel, France	CM-4
<b>Vlaconit</b>	Nat. resin base	m, thermoplastic	Ver. Isolatorenwerke A.-G., Berlin-Pankow	CM-4; K-4
<b>Victrolac</b>	Vinyl resin	m, records	RCA Victor Co., Camden, N. J.	CM-4
<b>Victron</b>	Polystyrene resin	m	Naugatuck Chemical Co., Naugatuck, Conn.	CM-4

Name	Composition	Forms, Uses	Company	Source
<b>Vigorit</b> (Vigorito)	PF	t	Uhlhorn Bros., London, E.C. 1; Dr. F. Raschig, G.m.b.H., Lud- wigshafen, Rhine, Germany	BP. 1931, 2, 552; AR337; CM-4; BPY
<b>Vimkite</b>	CA sheet on wire netting			<i>Plastics</i> , 1933, 9, 232; CM-4
<b>Vinarol</b>	Polyacetal		I. G. Farbenind. A.-G., Frankfurt, Germany	
<b>Vinnapas</b>	Polyvinyl ace- tate		Consortium für Electrochem- ische Ind., G.m.b.H. Germany; Dr. A. Wacker A.-G.	CM-4; J86
<b>Vinsol</b>	Pine by-product		Hercules Powder Co., Wilmington, Del.	CM-4
<b>Vinylite</b>	Vinyl resin	m, coatings	Carbide & Carbon Chemicals Corp., New York	CM-4; APV-3; <i>Ind. Eng. Chem.</i> , 1933, 25, 645
<b>Vinyloid</b>	Vinyl resins	Coatings	Carbide & Carbon Chem. Corp., New York	<i>Ind. Eng. Chem.</i> 1933, 25, 645
<b>Viralite</b>	Netting coated with cellulose acetate		Darlington Fencing Co., Ltd., London, E.C. 4	CM-4
<b>Viscold</b>	X, SR	m	Viscose Development Co., Ltd., England	KPM290; CM-4, BPY
<b>Viscoloid</b>	Pz	f	Du Pont Viscoloid Co., Leomin- ster, Mass., and Arlington, N. J.	CM-4
<b>Viskanol</b>	Hydrocarbon polymer	Coatings, adhe- sives	Advance Solvents & Chem. Corp., New York	
<b>Visking</b>	CA	P	Visking Corp., Chicago	CM-4; PGB-3
<b>Viskopius</b>	Aluminum naphthenate		Advance Solvents & Chem. Corp., New York	
<b>Vitrolux</b>	Cellulose com- position	Panes	W. & G. Baird, Ltd., England	CM-4, APV-2
<b>Vortex-Burt</b>	PF, F		Vortex Cup Co., Chicago	CM-1
<b>Vulcabeston</b>	Rubber-asbestos	Insulation	Colt's Patent Fire Arms Mfg. Co., Hartford, Conn.; Geo. H. Scholes & Co., Ltd., Manches- ter, England	KPM290; PGB-1
<b>Vulcalock</b>	Resin soln., con- tains Thermo- prene	Adhesive espe- cially for bond- ing rubber to metal	B. F. Goodrich Rubber Co., Akron, Ohio	<i>Chem. and Met.</i> , 1935, 42(7), 15
<b>Vulcoid</b>	PF	l, using vulcan- ized fiber	Continental-Diamond Fibre Co., Newark, Del.	CM-4
<b>Vulcoid</b>	Parchmentised cellulose, with aniline resin		Continental-Diamond Fibre Co., Newark, Del.	
<b>Vulcone</b>	Aniline-aldehyde		Soc. du Pont de Nemours	<i>Kunst.</i> , 1925, 15, 114
<b>Vydon</b>	Vinyl resin	Dentures	Lee S. Smith & Son Mfg. Co., Pittsburgh, Pa.	BP, 1933, 5, 79; CM-4
<b>Wacker Shellac</b>	Acetaldehyde resin-modified shellac		Dr. Alexander Wacker Ges., Münich, Germany	AR260, 266; CM-4
<b>Wahnerit</b>	PF	l	Elektro-Isolier-Industrie, G.m.b.H., Wahn, Germany	CM-4
<b>Walkerite</b>	PF	Denture	Dental Mfg. Co. Ltd., England	CM-4; <i>J.A.C.S.</i> , 1933, 55, 670
<b>Walonerit</b>	?	m	Elektro-Isolier-Industrie, G.m. b.H., Wahn, Germany	CM-4

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Name	Composition	Forms, Uses	Company	Source
<b>Wandrite</b>	PF		H. Wandrowsky, Berlin-Friedenau, Germany	PGB-2; CM-4; K-1
<b>Waterlite</b>	Styrene resin, PF		Watertown Mfg. Co., Watertown, N. Y.	CM-4; APV-2
<b>Wenjasit</b> (Wenjacite)	PF	t	Kunst-Rohstoff, A.-G., Hamburg, Germany	CM-4
<b>Westbury Ware</b>	PF, SR, X	m	Reliance Mfg. Co. Ltd., London, E. 17	CM-4; BPY
<b>Xantholith</b>	PF		Cie. Franc. Plinatus, Paris	CM-4
<b>Xillite</b>	PF	t	Italy	Plastics, 1930, 8, 589; CM-4; K-4
<b>Xylonite</b> (Xylonit)	Px	f	British Xylonite Co., London, England	CM-4; PGB-2
<b>Xylose</b>	Benzyl cellulose	Denture	"Bakelite" Dental Supplies, London, N. 3	BP. 1932, 4, 186; CM-4, BP1
<b>Yunos</b>	PF, F		Universal Electric Lamp Co., London, E.C. 2	CM-4
<b>Zalmite</b>	PF	m, s	Simmons Co., Kenosha, Wisconsin	CM-4; PGB-3
<b>Zellon</b> See Cellon	CA		Deutsche Celluloid Fabrik, Eilenberg, Germany	CM-4; PGB-1
<b>Zellwonet</b>	PF		Fabryka Kabli, Krakow, Poland	CM-3
<b>Zellwonet</b>		Creaseless textiles	Tootal, Broadhurst, Lee Co., Ltd., Glossop, England	CM-3
<b>Zyl</b>	PF		Magnasco Roggero & Co., Genoa, Italy	CM-1
<b>Zyl</b>	UF	t, m	Meunier (France)	CM-1
<b>Zyl</b>	X, aldehyde resins		Consortium für Elektrochem. Ind., München, Germany	CM-1



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